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A Method for the Sampling and Analysis of Polychlorinated Biphenyls (PCBs) in Ambient Air

Environmental Science and Engineering, Inc, Gainesville, FL

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A Method for Sampling and Analysis of Polychlorinated Biphenyls (PCB's) in Ambient Air

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A method has been developed for the sampling and analysis of polychlorinated biphenyls (PCBs) in air. An easily constructed, high-volume sampling system is em employed with porous polyurethane foam as the collection medium. The sample is collected at the rate of 0.6 to 1.0 m^3 per minute. Laboratory procedures described in this document permit the quantitative analysis of even the most volatile PCB species in an air sample. A perchlorination technique for the quantitative analysis of PCB has been adapted for use. The technique is shown to convert even the most volatile PCB species to decachlorobiphenyl for simple and direct quantitative analysis. Data is presented to show conversion efficiencies of a variety of PCBs to decachlorobiphenyl of 101 ± 6 percent over the range of 0.103 to 10.0 ug. A ruggedness test was conducted which indicates the proposed perchlorination technique can yield reliable interlaboratory results. The perchlorination technique is generally necessary for the analysis of low (i.e., less than 25 ng/m^3) airborne levels of PCB. The analytical method is effective for the analysis of airborne PCB levels within at least the range of 1 ng/m^3 to 50 ug/m^3. The mean collection efficiency for Aroclor 1016/1242 was 101 ± 10 percent for sampling periods of 20 minutes to 12 hours and air volumes of 16 to 720 cubic meters. Field tests of the method under a variety of ambient conditions are described.

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A METHOD FOR THE SAMPLING AND ANALYSIS OF POLYCHLORINATED BIPHENYLS (PCBs) IN AMBIENT AIR

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ABSTRACT

A method has been developed for the sampling and analysis of polychlorinated biphenyls (PCBs) in air. An easily constructed, high-volume sampling system is employed with porous polyurethane foam as the collection medium. The sample is collected at the rate of 0.6 to 1.0 m^3 per minute. Laboratory procedures described in this document permit the quantitative analysis of even the most volatile PCB species in an air sample. A perchlorination technique for the quantitative analysis of PCB has been adapted for use. The technique is shown to convert even the most volatile PCB species to decachlorobiphenyl for simple and direct quantitative analysis. Data is presented to show conversion efficiencies of a variety of PCBs to decachlorobiphenyl of 101 ± 6 percent over the range of 0.103 to 10.0 ug. A ruggedness test was conducted which indicates the proposed perchlorination technique can yield reliable interlaboratory results. The perchlorination technique is generally necessary for the analysis of low (i.e., less than 25 ng/m^3) airborne levels of PCB. The analytical method is effective for the analysis of airborne PCB levels within at least the range of 1 ng/m^3 to 50 ug/m^3. The mean collection efficiency for Aroclor 1016/1242 was 101 ± 10 percent for sampling periods of 20 minutes to 12 hours and air volumes of 16 to 720 cubic meters. Field tests of the method under a variety of ambient conditions are described. This report was submitted as part of fulfillment of contract 68-01-2978 by Environmental Science and Engineering, Inc. under sponsorships of the Environmental Protection Agency.

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1.0 INTRODUCTION

Polychlorinated biphenyls (PCBs) have been detected by numerous researchers in all environmental media. Significant levels of contamination have been detected in waters, aquatic sediments, soils, and biota. Data is conspicuously limited, however, for the assessment of airborne PCB contamination. Since the atmosphere may serve as both a transport medium for PCB from a source to the environment and as a mechanism for direct human exposure, it is important to evaluate airborne PCB levels. No commonly accepted method is presently available for the sampling of airborne PCB. Investigations were, therefore, undertaken to identify and evaluate a usable ambient air sampling method with adequate detection limit, sensitivity and specificity to reliably assess airborne pollution by this class of compounds. The purpose of this report is to describe one such method for the measurement of airborne levels of PCB and to present data documenting the performance of the method under laboratory and field conditions.

1.1 COMPLEXITY OF AIRBORNE PCB MEASUREMENT

There exist a number of complicating factors which must be taken into consideration in the measurement of airborne PCB levels. Principal among these are:

a. The term "PCB" applies, not to a single chemical species, but to a class of chemical compounds. These compounds are related by chemical structure and by degrees of halogen substitution on the molecule. PCB is seldom manufactured or used in the pure isomeric state. For industrial application, PCBs are marketed in the form of mixtures, each mixture containing a significant fraction of the 209 possible isomeric species. For example, Aroclor® 1242, a commercial PCB mixture, is comprised of 54 identified isomers (Hutzinger, Safe and Zitko, 1974). Such mixtures have been detected in numerous environmental media. The fact that a class of chemical compounds and not a single identifiable chemical species is to be detected and measured greatly multiplies the complexity of the chemical analysis in an already complex environmental medium such as the ambient atmosphere.

b. Our concern is with extremely low airborne concentrations of PCB. Measurements reported to date indicate ambient levels are in the ng/m^3 or part per trillion (ppt) range.

c. Not only are airborne PCB levels expected to be low, but they must be detected in the presence of a large number of other organic compounds which may be present in much higher concentrations than the PCB. Organic compounds from both natural and manmade sources will complicate PCB collection and analysis.

d. Analytical methods have been developed for the analysis of PCB in most environmental media. These methods generally employ gas-liquid chromatography (GC). They have been developed after years of laboratory work required to perfect extraction, concentration, cleanup, and analytical techniques. There are numerous variations to each of these techniques, but they all entail lengthy, exacting methods of sample handling and treatment. Since the present interest is with airborne PCB, it may be expected to be necessary to deal with the more volatile species in this class of compounds. The more volatile species have proven to be more difficult to handle analytically than the less volatile, or more highly substituted, PCB species, and hence, require even more attention to analytical detail.

e. The state-of-the-art of quantitation of PCB by gas chromatographic analysis is not well-developed. Currently used methods are subjective. This leads to considerable variability among analysts.

There has always been difficulty in accurately quantifying PCB present in environmental media. In most cases, the multipeak GC elution pattern observed after separation of pesticides and other interfering compounds by extensive extract cleanup procedures is subjectively compared to the elution pattern of a commercial PCB mixture. A decision is made as to what commercial product the sample elution pattern most closely represents. The quantity of PCB present is then calculated by comparison of several matching GC peaks between the sample and a known concentration of the commercial product. Inherent in this method of quantitation is the assumption that all PCB isomers are present in the sample in the same proportion as in the commercial mixture chosen for quantitation purposes.

There is no reason to believe the GC elution pattern of ambient airborne PCB would closely resemble that of a commercial product. The more volatile PCB species of a given commercial mixture would likely be selectively enriched in the airborne phase as compared to the solvent phase. This phenomenon of selective airborne enrichment of the lower-substituted PCB isomer has been demonstrated by Mieure (1975) for vapors above a standard Aroclor 1016 mixture. One would expect even greater apparent enrichment of more volatile species as samples are collected further from the source of the airborne contamination.

The most common method of PCB analysis, using the electron capture detector in conjunction with gas chromatography, introduces still another complicating factor. The response factor or sensitivity of the various PCB isomers in a given mixture will vary by several orders of magnitude depending upon not only the degree of chlorination, but on the position of the chlorine atom on the PCB molecule (Zitko, Hutzinger and Safe, 1971). The response is not linear with substitution. The analyst must, therefore, be absolutely certain he is comparing, for quantitative purposes, GC peaks generated by the identical isomer.

1.2 REQUIREMENTS OF A METHOD TO MEASURE AIRBORNE PCB

Any method which is selected for the measurement of airborne PCB must conform to a demanding set of performance criteria. The most important of these criteria are dictated by the anticipated difficulty in analyzing airborne PCB. These criteria are:

a. The selected method must incorporate the sampling of large volumes of air. To avoid excessively lengthy sampling periods, it was considered important that the sampling method chosen be a high-volume technique. This is necessary to achieve the desired low detection limit for the ambient atmosphere within a reasonable sampling period.

b. The chosen sampling method must demonstrate a high collection efficiency for airborne PCB. A sampling technique which approaches quantitative collection of the airborne PCB is essential to achieve the desired low detection limit, precision, and accuracy of the measurement.

c. Since one of the complicating factors which must be overcome in the measurement of ambient airborne PCB is the presence of other organic materials in the atmosphere, many in much higher concentration than the PCB, the sampling and analytical techniques must be specific to PCB. The difficulties encountered in accurately quantifying PCB in environmental media have been discussed. These difficulties are even more greatly magnified when contaminants, which are not of immediate interest, are present in the final analytical extract. When this is the case, the multipeak chromatogram is increasingly difficult to interpret.

d. It is desired to select a method that is relatively easy to perform and that lends itself to standardization. This applies to both the sampling activity in the field and to laboratory analytical procedures.

e. The selected method should permit qualitative assessment of the PCB present as well as quantitative assessment. It should be possible to ascertain the general distribution of the total PCB present according to species. For example, if the ambient PCB should resemble a specific commercial mixture, this information is desired in order to evaluate the potential source of the contamination and to assess the potential health and environmental hazard.

f. It would be highly preferred that the selected method had been shown by previous researchers to perform well. This would greatly reduce the effort necessary to adapt the method of routine use.

2.0 RESULTS AND DISCUSSION

A review was conducted of potential sampling and analytical techniques for airborne organic pollutants that would apply to PCB. A sampling method and analytical methods were selected for evaluation based on the reported experience of previous researchers. A high-volume sampling method using polyurethane foam as the collection medium was considered to be the candidate method that most closely matched the desired criteria. This sampling method was combined with analytical methods reported by researchers to be effective in determining low concentrations of PCB in environmental media, to arrive at a complete step-by-step procedure for assessing airborne PCB concentrations.

The selected method was evaluated in the laboratory and in the field. The evaluation consisted of an analytical recovery study, a sampling efficiency study, an analytical ruggedness test, a number of preliminary field tests, and a final field test. The analytical recovery study was necessary to establish procedures and to overcome difficulties encounterd in the laboratory analysis of the airborne samples collected on polyurethane foam so that quantitative results could be achieved. Collection efficiency studies were conducted to identify the limits of the high-volume sampling technique selected. Preliminary field tests were necessary to obtain experimental samples of the ambient atmosphere during method development. These field data were used to evaluate the method from the standpoint of the practicality of application under field conditions. A final field test was conducted to demonstrate the application of the method.

2.1 SELECTION OF THE SAMPLING METHOD

It was desired to select a sampling technique for airborne PCB that has been evaluated by other researchers and that conforms as closely as possible to the performance criteria set forth above. A review of published literature indicated some experience had been reported in the use of wet impingers, solid adsorbents, silicone oil, and polyurethane for the collection of airborne PCB.

Harvey (1974) employed a sampling device consisting of a tube packed with silicone-oil coated ceramic saddles through which a large volume of air can be drawn at the rate of 0.6 m^3/min. Harvey determined the colllection efficiency of this method using trichlorobiphenyl, hexachlorobiphenyl, and Aroclor 1254. He tested the collection efficiency by applying known quantities of these PCB species and the commercial mixture to a glass fiber filter which preceeded the adsorbent medium in the collection system. The average collection efficiency was 70 percent. Concentrations in the ambient atmosphere over the western North Atlantic of 0.05 to 5.3 ng/m^3 were reported by Harvey using this method. He expressed the opinion that the method can only approximate PCB concentrations in ambient air.

Giam, Chan, and Neff (1975) recommend a method for the detection of PCB in air which makes use of a solid adsorbent, Florisil, packed in a short glass column. Air is pumped through this column at the rate of 2 to 4 l/min. By placing several of these sample columns in series, it was found that PCB spiked onto the first column was retained only on the first column for sampling time as long as 60 hours. Using this arrangement to sample laboratory atmosphere, Giam, Chan, and Neff reported levels of 35 to 90 ng/m^3 PCB. No attempt was made to identify the PCB species present.

Bidleman and Olney (1974a) reported ambient concentrations of PCB over the western North Atlantic and Rhode Island of 0.21 to 9.4 ng/m^3.

These researchers (Bidleman and Olney, 1974b) devised a high-volume sampling method employing polyurethane foam as the collection medium. Cylindrical polyurethane foam plugs, of 10 cm thickness, are placed in a high-volume air sampler behind the standard filter holder. Air is drawn through the sampling apparatus at the rate of 0.5 to 1.0 m^3/min. The authors evaluated the collection efficiency of this medium by placing the sampling device near the source of tri-, tetra-, and pentachlorobiphenyl. The device was equipped with two polyurethane foam plugs. A glass fiber filter was placed in the filter holder. In this manner, these researchers determined less than 1 percent of the PCB isomers tested was trapped on the glass fiber filter and 96 to 99 percent of the total collected was trapped on the first polyurethane foam plug. Bidleman and Olney at the same time, and in the same manner, evaluated the collection efficiency of Greenburg-Smith impinger systems charged with ethylene glycol. They found this impinger system trapped 75 to 82 percent of the total tetra- and pentachlorobiphenyl while that remaining passed through the sampling system. Bidleman and Olney concluded, based on this preliminary evaluation, that the polyurethane foam was an effective collection medium for airborne PCB.

The high-volume sampling method of Bidleman and Olney (1974b) was selected for evaluation and application to assessing ambient airborne levels of PCB. Of the methods investigated by previous researchers, this one appeared to most closely meet the performance requirements set forth above for the following reasons:

a. It is a high-volume method that should provide the capacity of determining low ambient levels of airborne PCB without excessively long sampling periods.

b. A high collection efficiency has been demonstrated for the tri-, tetra-, and pentachlorobiphenyl species.

c. The polyurethane foam used as a collection medium has been used for the concentration of PCB in natural waters. It was selected for this purpose, partly because it demonstrates a degree of selectivity for PCB. If this proved to be true for airborne organic pollutants, it would be of considerable advantage, since this technique would provide a means to selectively increase the ratio of PCB to other organic materials which may interfere analytically in the sample.

d. The apparatus and the manipulation required in the field are relatively simple and straightforward, so that it has potential for adaption to routine monitoring use.

e. The method should enable both a qualitative assessment of the species distribution of the PCB present and a quantitative assessment of the amount of PCB present.

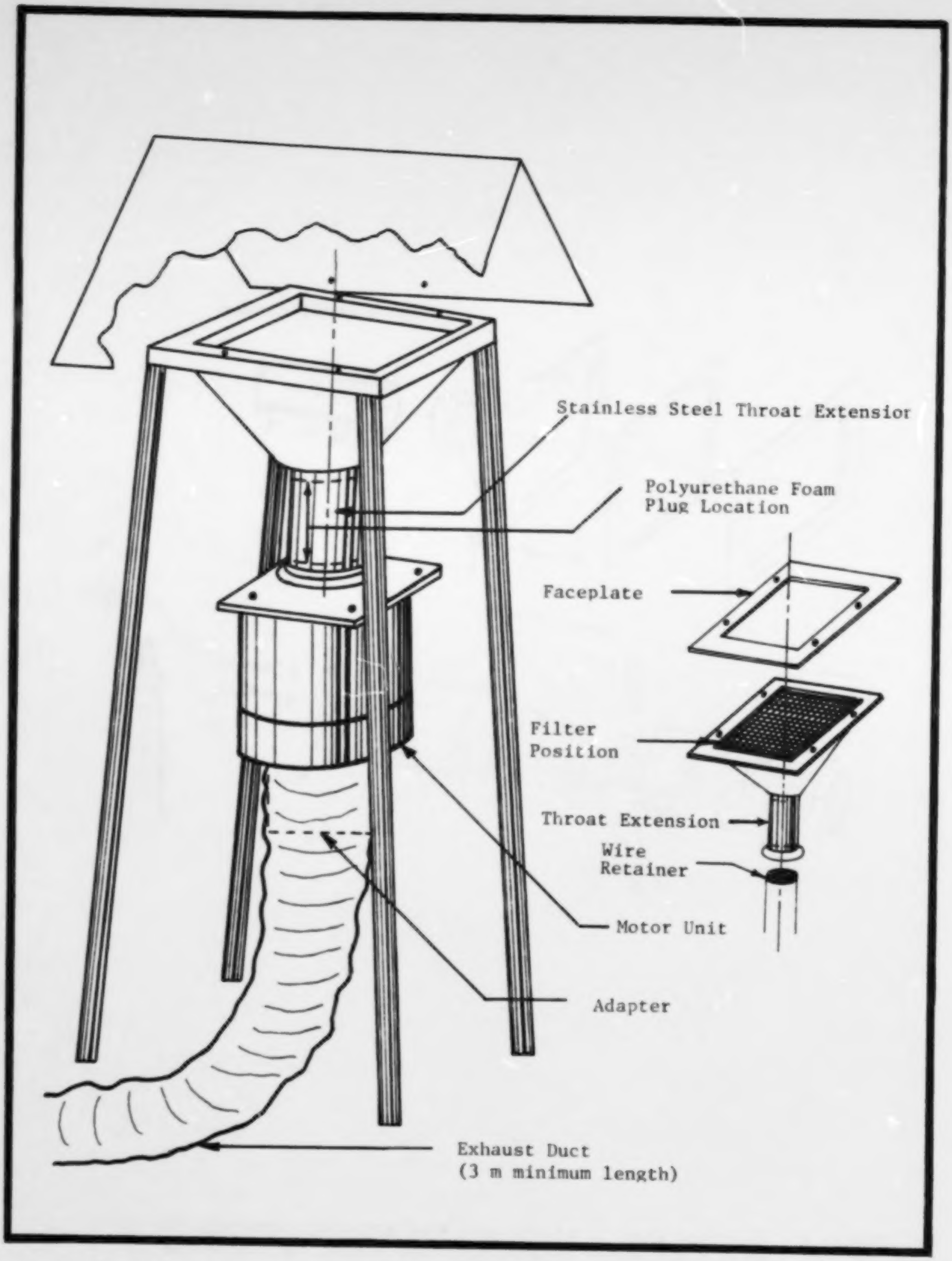
f. Bidleman and Olney (1974b) have conducted a preliminary evaluation of the method and expressed confidence in its application to assess ambient airborne contamination.

Several authors (Rhoades, et al., 1977; Rice, et al., 1976; Lewis, et al., 1977) have recently reported on experience they have gained in the laboratory testing and application of polyurethane foam for the sampling of PCB in ambient air. Margeson (1977) discusses the state of the art for ambient airborne PCB measurement.

2.2 DESCRIPTION OF THE SAMPLING APPARATUS

A sampling apparatus similar to that used by Bidleman and Olney (1974b) was designed using readily available equipment. A number of modifications were incorporated into the system to improve performance as a result of laboratory and preliminary field evaluation. The sampling apparatus, including all modifications, is illustrated in Figure 1. Figure 2 is an exploded view of the sampler. This apparatus was used for all evaluations reported in this document.

The basic sampling system is a modification of a standard high-volume sampling apparatus. These units are commonly used for airborne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Polyurethane Foam
Plug Location
Faceplate
Filter
Position
Throat Extension
Wire
Retainer
Motor Unit
Adapter
Exhaust Duct
(3 m minimum length)

Figure 1. Assembled sampler and shelter with exploded view of the filter holder.

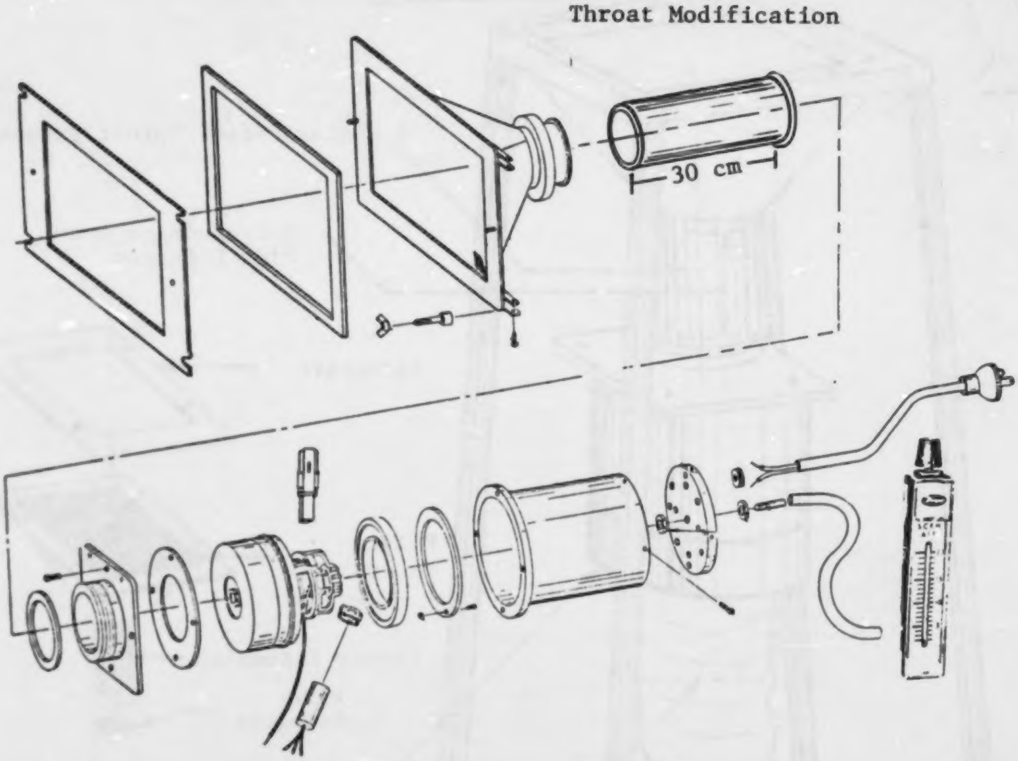

Throat Modification
30 cm

Figure 2. Exploded view of hi-vol sampling apparatus designed for use with a rotometer showing modified throat to accomodate polyurethane foam plugs.

particulate sampling. They consist of a stainless steel filter holder and throat assembly coupled to a high capacity centrifigal blower. The standard high-volume sampler used is manufactured by General Metal Works of Cleves, Ohio. It was modified by removal of the 3 cm long by 8 cm diameter cylindrical throat assembly between the filter holder and the blower housing and replacement by a throat assembly of similar design but 30 cm in length. The extended throat assembly was welded to the filter holder assembly. This provided a space for placement of the polyurethane collection medium. The neoprene seal located on the backside of the faceplate was removed and all adhesive material was scrupulously removed with organic solvents. Teflon tape was then used to provide a seal between the faceplate and the filter holder. These modifications resulted in a high-volume sampling system which contained only stainless steel and teflon components and surfaces ahead of the collection medium in the air stream. This was considered important to eliminate the potential for contamination of the sample by organic materials that may leach from the seating gasket normally used.

Initially, a standard high-volume sampler housing was used to support the apparatus. This proved unsatisfactory for two reasons. It was large, cumbersom, and difficult to transport. The blower motor operates under greater load than the conventional high-volume sampling use, and hence, tended to heat the enclosed sampler housing to an excessive degree. Elevated temperatures were considered potentially disadvantageous to the capability of the adsorbent medium to retain the PCB. A simplified, open construction sampler supporting stand was therefore designed. The basic design of this supporting stand is shown in Figure 1. Four legs constructed of steel pipe are fitted into couplings welded to a rectangular steel support ring. This support ring is fashioned to the dimensions of the filter holder assembly. The sampling apparatus is suspended in this support assembly. An aluminum sheet cover is positioned over the filter assembly and supported by threaded bolts welded to the support ring. The cover is attached to these bolts with wing nuts. This cover protects the glass fiber filter and the collection medium from rainfall in the same manner a conventional high-volume sampler housing is used.

High-volume samplers are normally operated from a conventional 60-cycle, 120-volt power supply. With a glass fiber filter in place, a typical sampler will draw air at approximately 1.7 m^3/min. The air flow rate is reduced to approximately 1 m^3/min with the polyurethane foam inserted into the throat and the glass fiber filter in place. Better flow control is achieved by use of a motor speed controller. A potentiometric controller or variac of suitable capacity should be used. A flow rate curve is generated for each individual sampler using the various size orifice plates supplied by the manufacturer. After this curve is plotted, the flow may be determined at any time by measurement of the exhaust pressure, in inches of water, using a manometer, rotometer, or calibrated gauge. The flow calibration is described in the Code of Federal Regulations (1975). For the purpose of sampling airborne PCB, a flow rate of 0.8 m^3/min was found to be suitable.

Some difficulty was experienced during initial sampler runs with the movement of the polyurethane foam down the throat assembly and seating against the inner housing assembly of the blower. The polyurethane foam could not enter the blower, and hence, this was not an immediate problem. However, it was considered a simple precaution to place a retainer in the throat assembly to prohibit the polyurethane foam from moving. This simple retainer device is shown in the exploded view in Figure 1. It seats on the inner blower housing and keeps the polyurethane approximately 5 cm above the blower intake. A piece of rigid hardware cloth would serve the same purpose.

Lewis and Zimmerman (1976) have reported the existence of a capacitor containing polychlorinated naphthalenes (PCN) in the motor assembly of certain standard high-volume samplers. When this unit is used for sampling PCB, using polyurethane foam plugs, PCN is found on the plugs. This implies the high-volume samplers used recirculate at least a portion of the sampled air. Significant air recirculation will result in low analytical results of the air sampled. In addition, PCN contamination severely interferes with both qualitative assessment and quantitative analysis of PCB. Recirculation must be prevented. This is accomplished by placing an exhaust duct three or more meters in length on the high-volume motor housing, as shown in Figure 1. Collapsible ducting is ideal for this purpose. In this way, the sampler exhaust can be located remote from the sampler intake to prohibit any opportunity for recirculation.

The high-volume samplers used throughout the laboratory investigations and field studies reported in this document do not contain the capacitor discussed by Lewis and Zimmerman (1976). Only samplers without the PCN-containing capacitor should be used.

A 20 cm x 25 cm glass fiber filter (Gelman Type A) is placed in the filter holder assembly for each sample run. The purpose of this glass fiber filter is not to separate particulate from gaseous PCB in ambient air, since this is not considered possible with a compound of insufficiently low vapor pressure, but to keep airborne particulate from embedding in the polyurethane foam. The glass fiber filter is normally analyzed along with the polyurethane after sample collection. Experience has shown, in most cases, that a significant amount of PCB is seldom retained on the glass fiber filter. Once this is established, it is not necessary to include the glass fiber filter in the analysis.

The collection medium used is a commercially available polyurethane foam material. For purposes of this study, a 7.6 cm thick sheet of the material of density 0.025 g/cc was obtained. Cylindrical plugs of 9 cm diameter are cut from the foam sheet. The plugs are cut oversize so that they fit snugly into the sampler in such a manner that air cannot bypass them. Three polyurethane foam plugs, each 7.6 cm in thickness, were used, for a total thickness of 23 cm, for most of the studies conducted. The extensive polyurethane foam cleanup procedures that must be followed before the material is used will be discussed in a later section of this report.

2.3 ANALYTICAL PROTOCOL

The step-by-step procedure recommended for the analysis of ambient airborne PCB is included as Appendix A to this report. This procedure is drawn from the technical literature, personal contact with persons knowledgeable in the field, and both laboratory and field experience. The purpose of this chapter is to relate experience gained during development of the method.

Figure 3 is a flow diagram of the analytical scheme. The procedure consists of preparation of materials, field sampling, extraction, concentration, cleanup, and gas chromatographic analysis. To avoid the difficulty and uncertainty in accurately quantifying the PCB present in a sample, it is often necessary to employ the perchlorination technique developed by Armour (1973). Considerable effort was applied to adopting this technique for routine use in quantitation of ambient airborne PCB. Some modifications of the perchlorination technique were necessary to achieve quantitative derivization of ambient airborne PCB.

2.3.1 Cleanup of Materials and Apparatus

It has been emphasized many times by numerous researchers that PCB are ubiquitous in the environment. They are present in the laboratory atmosphere, on glassware, and occasionally as contaminants in chemical reagents. Strict attention must be given to every detail of sample handling in order to avoid PCB contamination. It was found necessary to employ rather extensive cleanup measures to avoid PCB contamination from materials and apparatus. All materials that come into physical contact with the samples are sequentially cleaned by detergent wash, tap water rinse, deionized water rinse, acetone rinse, petroleum ether rinse, and heating to remove any residual organics. This applies to the sampling system, to glassware, aluminum foil, and any items used to handle the polyurethane foam.

The polyurethane foam that is used as an adsorbent medium requires extensive cleanup by solvent extraction in a soxhlet extraction apparatus. Extraction is performed with nanograde hexane for a period of 12 hours.

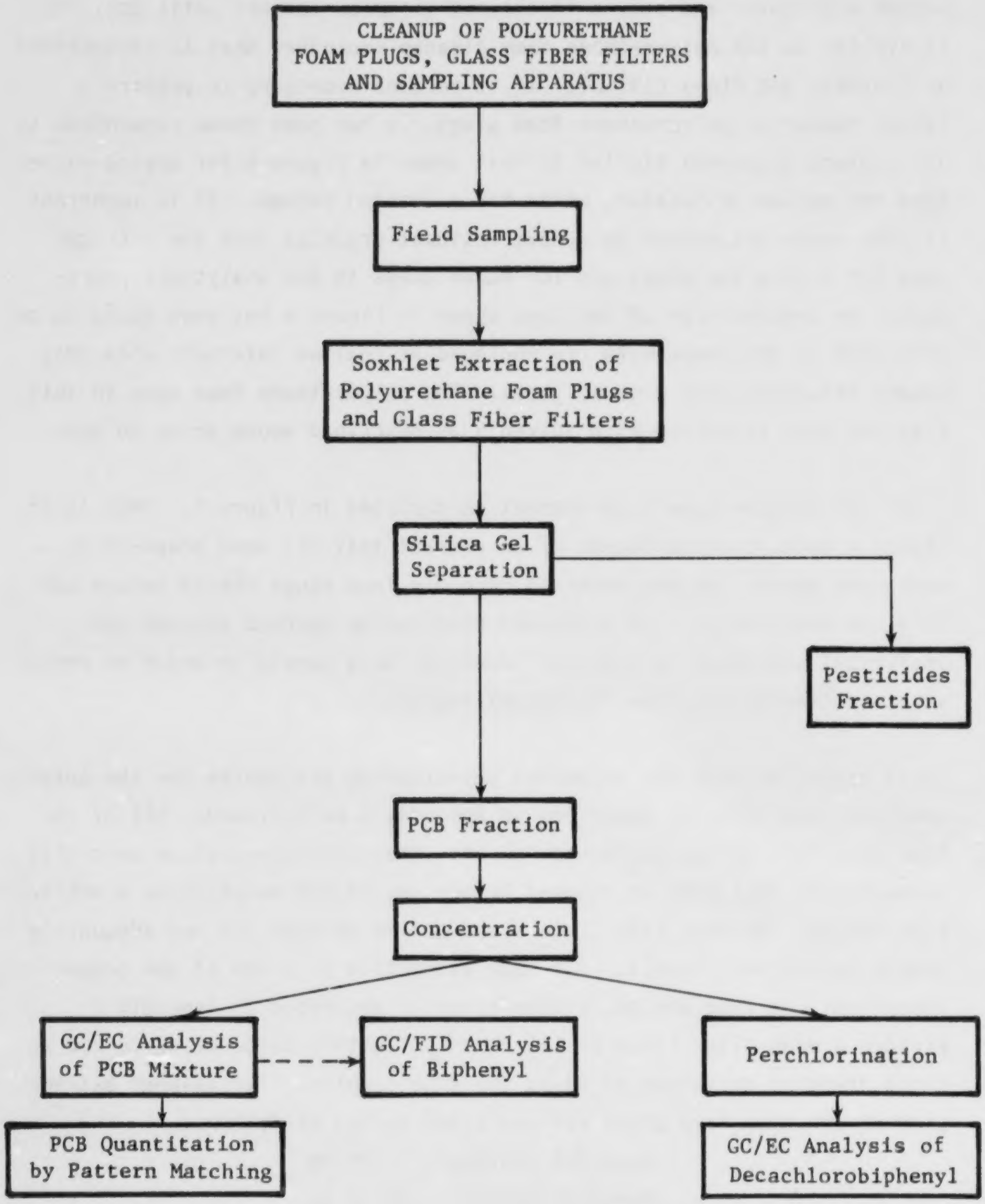

CLEANUP OF POLYURETHANE FOAM PLUGS, GLASS FIBER FILTERS AND SAMPLING APPARATUS
Field Sampling
Soxhlet Extraction of Polyurethane Foam Plugs and Glass Fiber Filters
Silica Gel Separation
Pesticides Fraction
PCB Fraction
Concentration
GC/EC Analysis of PCB Mixture
GC/FID Analysis of Biphenyl
Perchlorination
PCB Quantitation by Pattern Matching
GC/EC Analysis of Decachlorobiphenyl

Figure 3. Analytical scheme for PCB in ambient air.

Following this, they are dried with organic-free nitrogen in a heated vacuum desiccator and sealed in cleaned glass containers until use. This is similar to the polyurethane foam cleanup procedure that is recommended by Bidleman and Olney (1974b). If it becomes necessary to prepare a larger number of polyurethane foam plugs, it has been found convenient to use a glass apparatus similar to that shown in Figure 4 for drying rather than the vacuum desiccator, which has a limited volume. It is important to take every precaution to remove residual organics from the nitrogen used for drying the plugs and for other steps in the analytical procedure. An organic trap of the type shown in Figure 4 has been found to be effective if the components are replaced at routine intervals when they become saturated with organic gases. The polyurethane foam used in this trap has been extracted with solvents as described above prior to use.

A typical polyurethane foam extract is depicted in Figure 5. This is an electron capture chromatogram of an extract that has been prepared as described above. It was selected randomly from plugs stored before use in glass containers. The unexposed plug can be carried through the analytical procedure in a manner identical to a sample in order to demonstrate contamination-free laboratory procedures.

It is essential that the extensive pre-cleaning procedures for the polyurethane foam plugs as described in Appendix A be followed. All of the foam materials tested contained PCB and other electron capture sensitive contaminants that must be removed before use of the material as a collection medium. Shorter than 12-hour extraction periods did not adequately reduce contaminant levels. A 5-hour extraction of plugs of the proper dimensions cut from the stock foam material described in Appendix A yielded a mean blank value of 113 ng as DCB with a range of 42 to 200 ng and a standard deviation of 58 ng for five samples. Twelve-hour extraction of the same five plugs yielded blank values as follows:

Mean DCB residual	54 ng
Range of values	30-78 ng
Standard deviation	9 ng

Both the mean residual DCB and the range of values from one plug to another is reduced to manageable levels by 12-hour extraction. The residual DCB level (blank value) for each lot of polyurethane foam plugs that are prepared for sample collection must be determined before they are used in order to validate the adequacy of the pre-cleaning procedure.

Polyurethane foam plugs may be reused after sample extraction for collection of further samples by simply drying and returning to glass containers for storage. It is not necessary to repeat the 12-hour soxhlet extraction if the plug is not exposed to contamination.

The glass fiber filter (Gelman Type A) is pre-conditioned by heating for several hours to remove any organics present. These filters should not be stored in cardboard boxes or manila envelopes, since these materials and other paper products sometimes have very high levels of PCB contamination. A typical chromatogram of a filter blank is reproduced in Figure 6.

2.3.2 Field Sampling

Field sampling procedures are sufficiently straightforward that they can be performed without undue burden. It is necessary, however, that the individual responsible for sampling be conscientiously aware of the potential for PCB contamination and take routine precautions to avoid it.

Recirculation of exhaust from the sampling apparatus to the intake has been discussed. This is a problem that must be avoided by placement of the end of the exhaust duct so that recirculation is unlikely to occur. An exhaust duct 3 m in length has been found to be effective; however, if there is any question concerning the possibility of recirculation in a given situation, a longer exhaust duct is recommended. Collapsible ducting of the type used to vent household clothes dryers is ideal for this purpose.

The placement of pre-cleaned polyurethane foam plugs in the sampling apparatus is done at the sampling location. Only pre-cleaned metal tongs

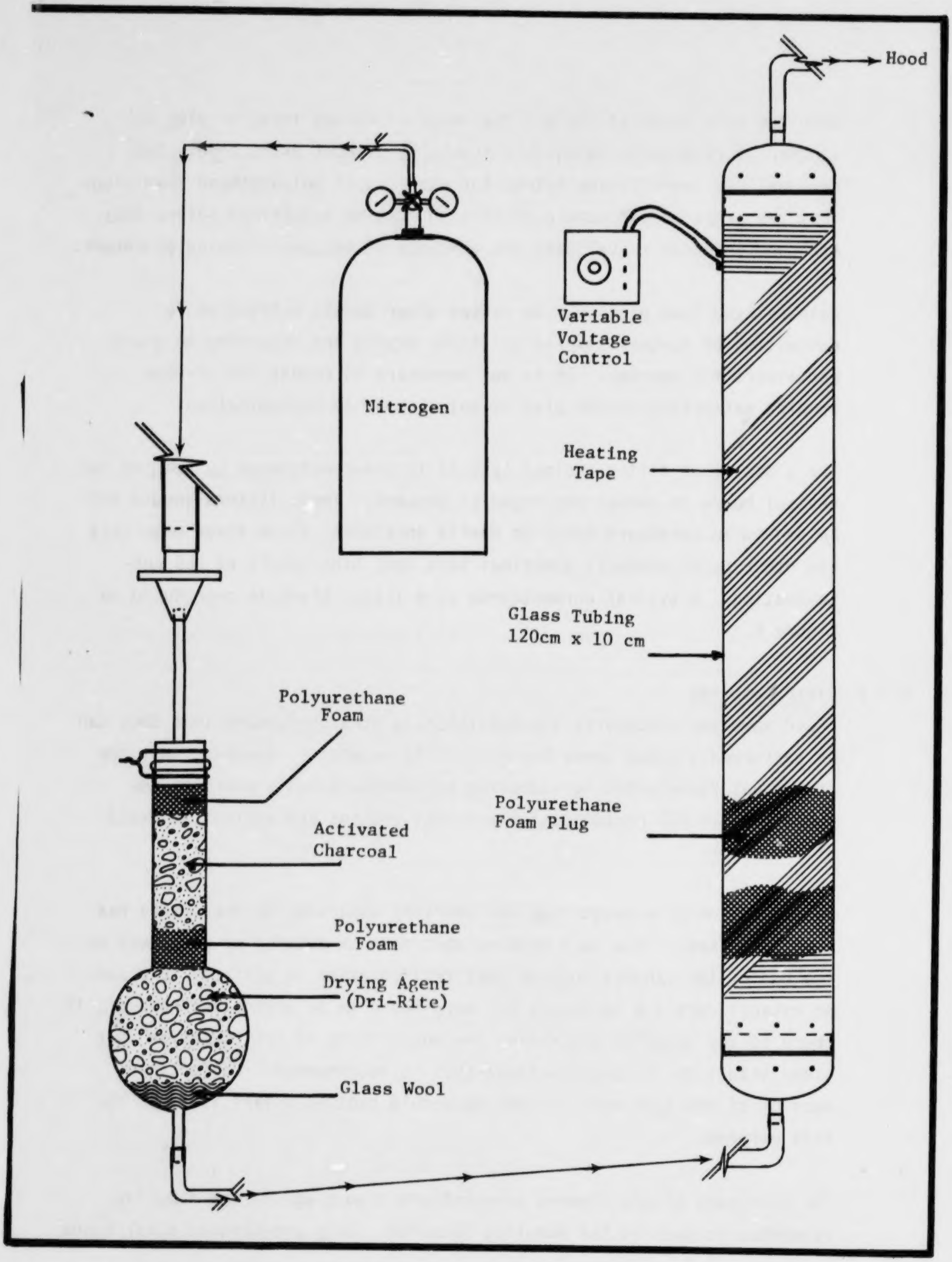

Hood
Variable
Voltage
Control
Nitrogen
Heating
Tape
Glass Tubing
120cm x 10 cm
Polyurethane
Foam
Activated
Charcoal
Polyurethane
Foam Plug
Polyurethane
Foam
Drying Agent
(Dri-Rite)
Glass Wool

Figure 4. Apparatus for drying polyurethane foam plugs.

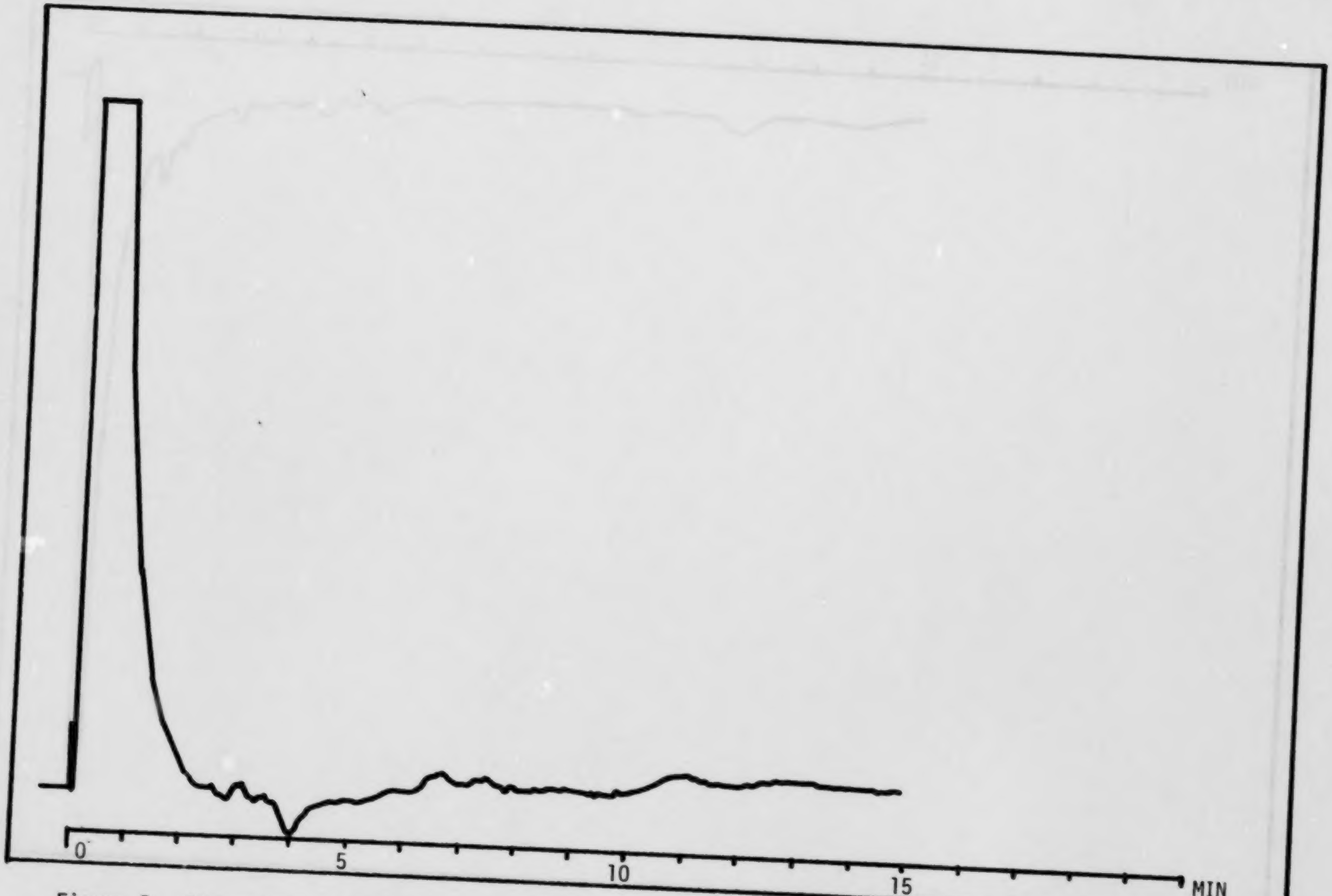


Figure 5. Chromatogram of a typical polyurethane foam extract at recorded attenuation 4 x 10^{-9}.

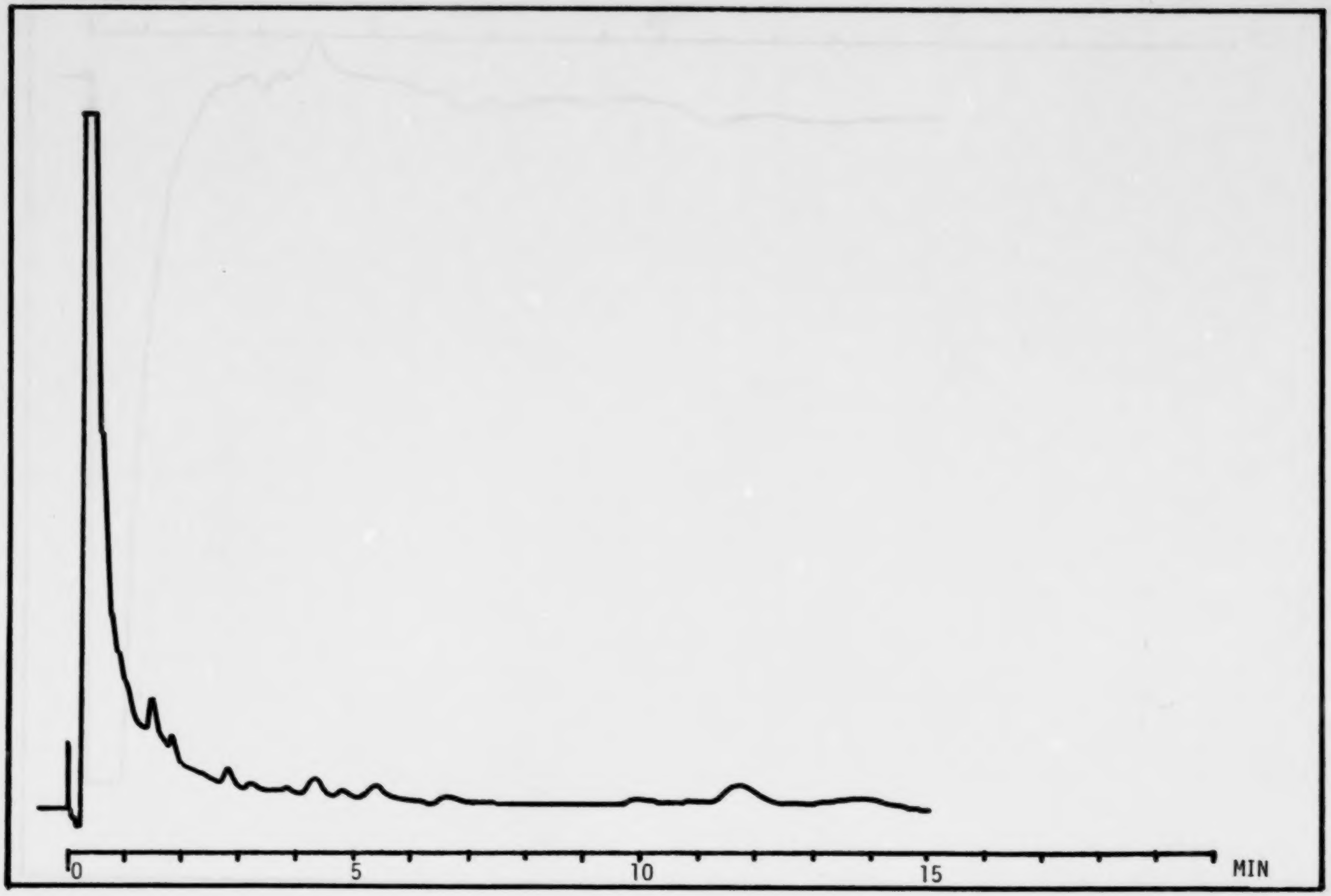


Figure 6. Chromatogram of a typical glass fiber filter (Gelman Type A) extract at recorder attenuation 4 x 10^{-9}.

are used to handle the plugs. When plugs are placed in the apparatus, the individual should assure they fit snugly to avoid any possibility of leaks around them. There should be a minimum of exposure of the cleaned plugs to the laboratory or ambient atmosphere. Immediately after sampling is complete, the polyurethane foam plugs are removed from the sampling apparatus and returned to the appropriately-labeled storage container for transport back to the laboratory. The glass fiber filter is handled in the same manner. When storage is necessary, it is preferable to keep the exposed plugs in the dark and under refrigeration in order to avoid any decomposition that may possibly take place.

2.3.3 Sample Extraction

Exposed polyurethane foam plugs are transferred to a soxhlet extraction apparatus and extracted for 3 hours with nanograde hexane. The glass fiber filter is extracted in the same manner as the plug. All plugs may be extracted together; they may be extracted separately and combined; or the glass fiber filter and the plugs may be analyzed separately. The polyurethane foam plugs can be reused if they are immediately dried in the proper manner and returned to storage in a sealed glass container. Even high concentrations of PCB (e.g., 128 ug as DCB) spiked onto a plug were quantitatively removed during a 3-hour extraction period.

Contamination of the sample was sometimes noted when the paper thimbles normally used in a soxhlet extraction apparatus were employed. It was found that the extractors performed satisfactorily without these thimbles and they were subsequently eliminated. Another point of caution is worth mentioning. An interference problem was encountered in the use of boiling chips ("Boileezers" marketed by Fisher Scientific Co.) in the soxhlet extraction step. Broken glass which has been heated to remove organics serves as a most satisfactory boiling aid without causing interference problems.

2.3.4 Sample Concentration

Larger volumes of sample extract are concentrated satisfactorily using a Kuderna-Danish evaporator. When it is necessary to reduce extract volume to less than 5 ml, a modified micro-Snyder apparatus is used. Extreme caution must be exercised to avoid evaporation of any sample to dryness. In the early phases of evaluation of the laboratory procedures, excellent recovery efficiencies (average 104 percent) were achieved with Aroclor 1260. Since airborne PCB is likely composed of more volatile species than those present in Aroclor 1260, analytical recovery studies were conducted using Aroclor 1016. This mixture contains principally di-, tri-, and tetrachlorobiphenyls. Recovery efficiencies were found to be erratic and poor. Step-by-step evaluation of the analytical technique isolated the problem to two steps in the procedure where the sample extract was evaporated to "near dryness." During these steps, it was found that a significant amount of the dichlorobiphenyl present in Aroclor 1016 was lost by volatilization resulting in modification of the chromatographic pattern. This, of course, would introduce serious error in the quantitation of airborne PCB. The analytical procedure was, therefore, modified to eliminate procedural steps resulting in the evaporation of sample extracts to dryness or "near dryness." Acceptable analytical recovery efficiencies (average of 97 percent) were subsequently achieved with Aroclor 1016 using the modified procedures.

2.3.5 Sample Cleanup

The silicic acid cleanup procedure developed by Snyder and Reinert (1971) is employed to remove chlorinated pesticides and other interfering substances from the sample. This technique is not effective in eliminating DDE or toxaphene.

The sulfuric acid cleanup procedure of Murphy (1972) was found to remove a significant number of contaminants from certain of the sample extracts; however, it was not found to be necessary to use a sulfuric acid cleanup step routinely.

2.3.6 GAS CHROMATOGRAPHIC ANALYSIS

Analysis was conducted on a Varian 2760 gas chromatograph using a tritide foil electron capture detector. A 1.5%/1.95% OV-17/QF-1 packed glass column was found to be suitable. Confirmation was performed on a 4%/6%

SE-30/OV-210 column. Operating conditions for both these columns are described in the appendix. Several analyses were also confirmed by gas chromatography/mass spectrometry (GC/MS) using a AEI 30 (Associated Electronic Industries) instrument. The OV-17/QF-1 column was used with this instrument under the same operating conditions as described in the appendix, with the exception that helium was used as the carrier gas in place of nitrogen.

The importance of confirmation of peaks cannot be overstressed. This can be demonstrated by the following two figures. The sample is one of the initial field samples of urban atmosphere. The chromatogram is complicated by numerous peaks which could not be identified as PCB. Figures 7(a), (b), and (c) are chromatograms of the first, second, and third polyurethane foam plugs, respectively, as they are located in the sampling apparatus. Figure 7(d) is a chromatogram of Aroclor 1221 on the same column. Those peaks indicated by a "●" match corresponding peaks in Aroclor 1221 and/or Aroclor 1016. The first major apparent PCB peak, eluting at 1.33 minutes, appears to be present in roughly equivalent amounts on all three plugs indicating a poor collection efficiency. This did not seem consistent with other data, so the sample was run on the confirmatory GC column. Figure 8(a) is a chromatogram of the first plug on the confirmatory column. Figure 8(b) is a chromatogram of Aroclor 1221 on the same column. 2-Monochlorobiphenyl (2-MCB), 4-monochlorobiphenyl (4-MCB), 2,2'-dichlorobiphenyl (2,2'-DCB) and 2,4-dichlorobiphenyl (2,4-DCB) have been identified by comparison with these pure PCB isomers.

The peak which appeared to match 2-MCB on the OV-17/QF-1 column, was not confirmed on the SE-30/OV-210 column. Its position falls between the peaks eluting at 1.18 minutes and 1.49 minutes. 2-MCB was not present at all. This was later confirmed by GC/MS analysis.

2.3.7 Perchlorination

Quantitation of PCB in environmental samples is sometimes an extremely difficult and, unfortunately, often an inexact procedure. There exists little difficulty in those cases where the GC elution pattern closely

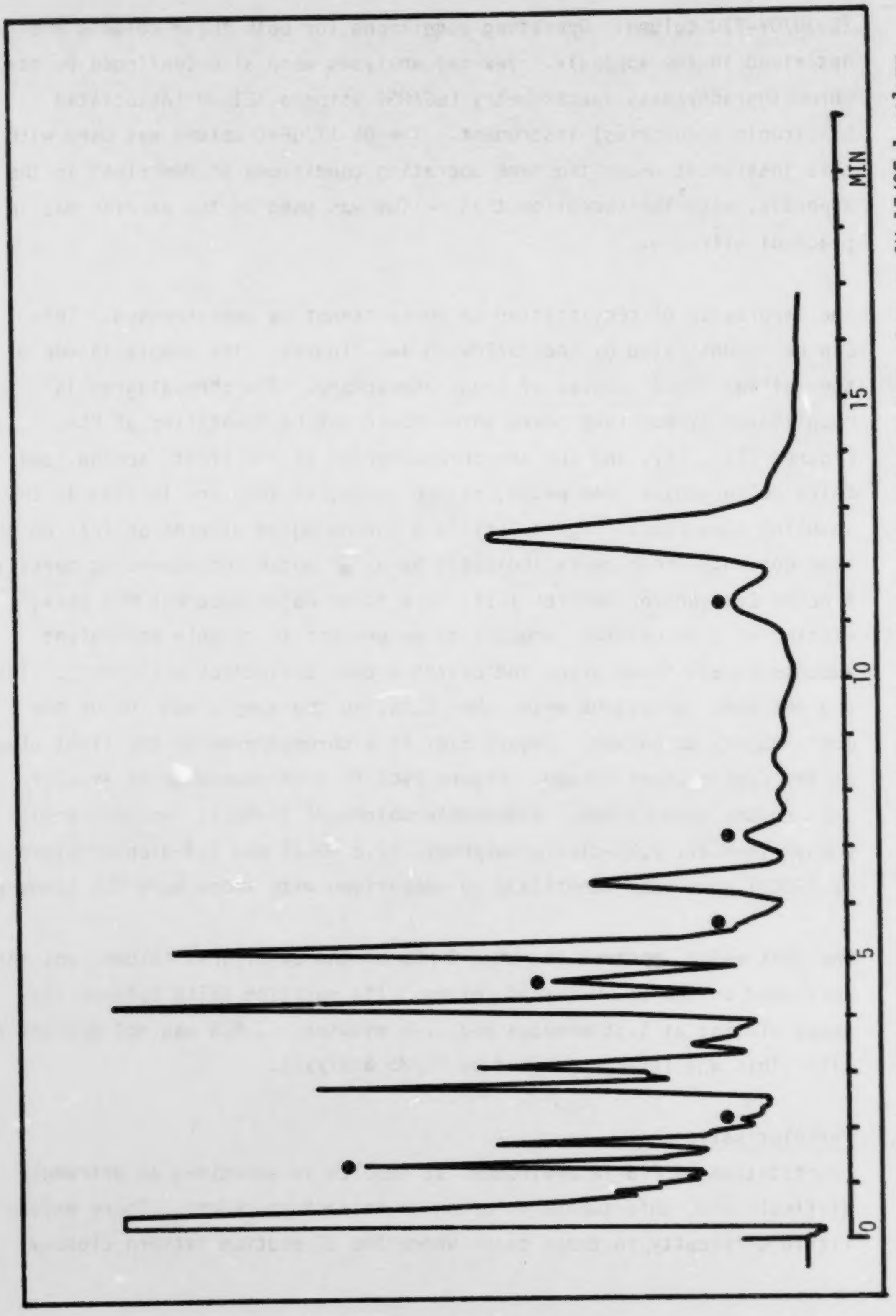


Figure 7(a). Chromatogram of an urban air sample, first polyurethane foam plug on OV-17/QF-1 column.

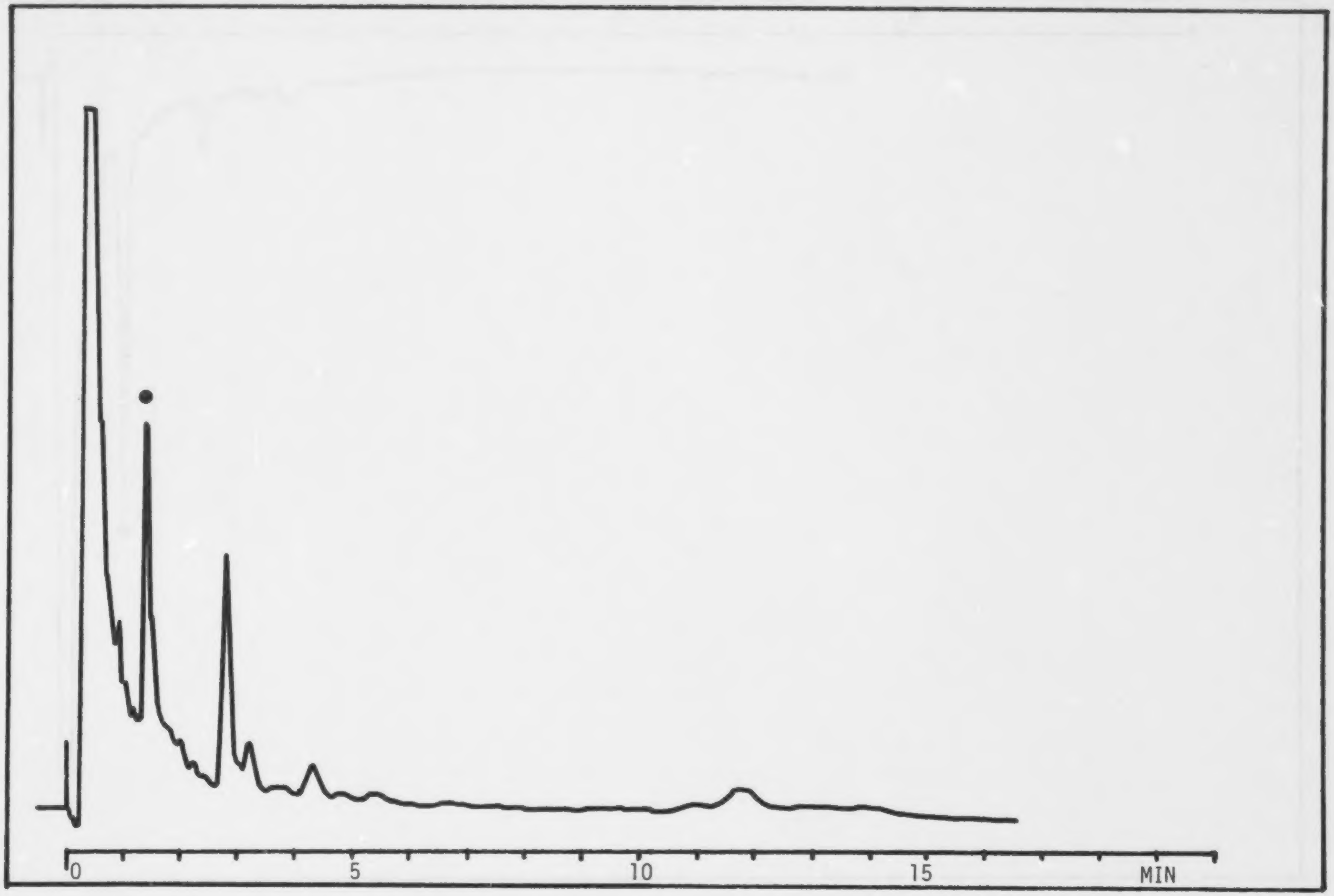


Figure 7(b). Chromatogram of second polyurethane foam plug on OV-17/QF-1 column.

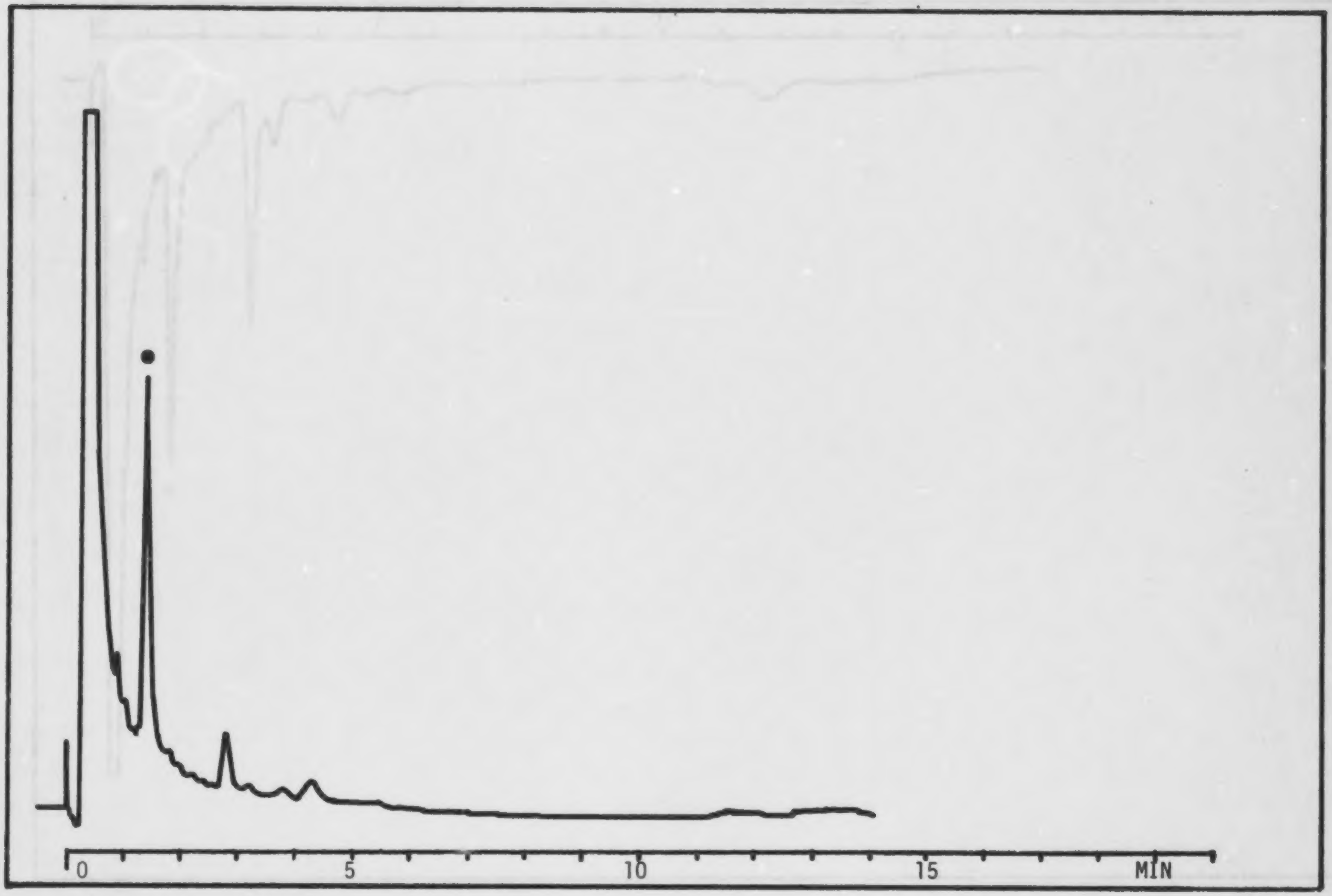


Figure 7(c). Chromatogram of third polyurethane foam plug on OV-17/QF-1 column.

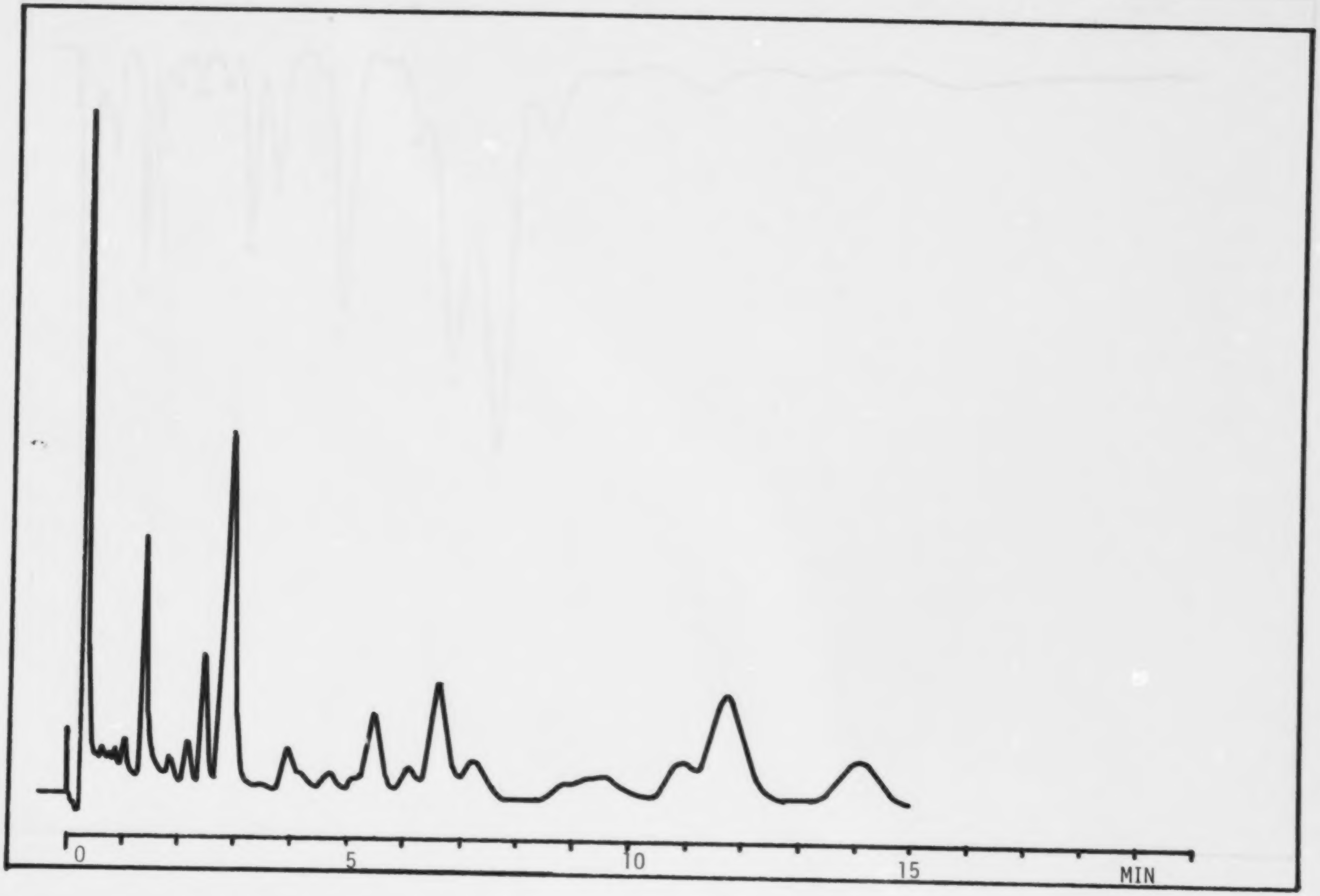


Figure 7(d). Aroclor 1221 on OV-17/QF-1 column.

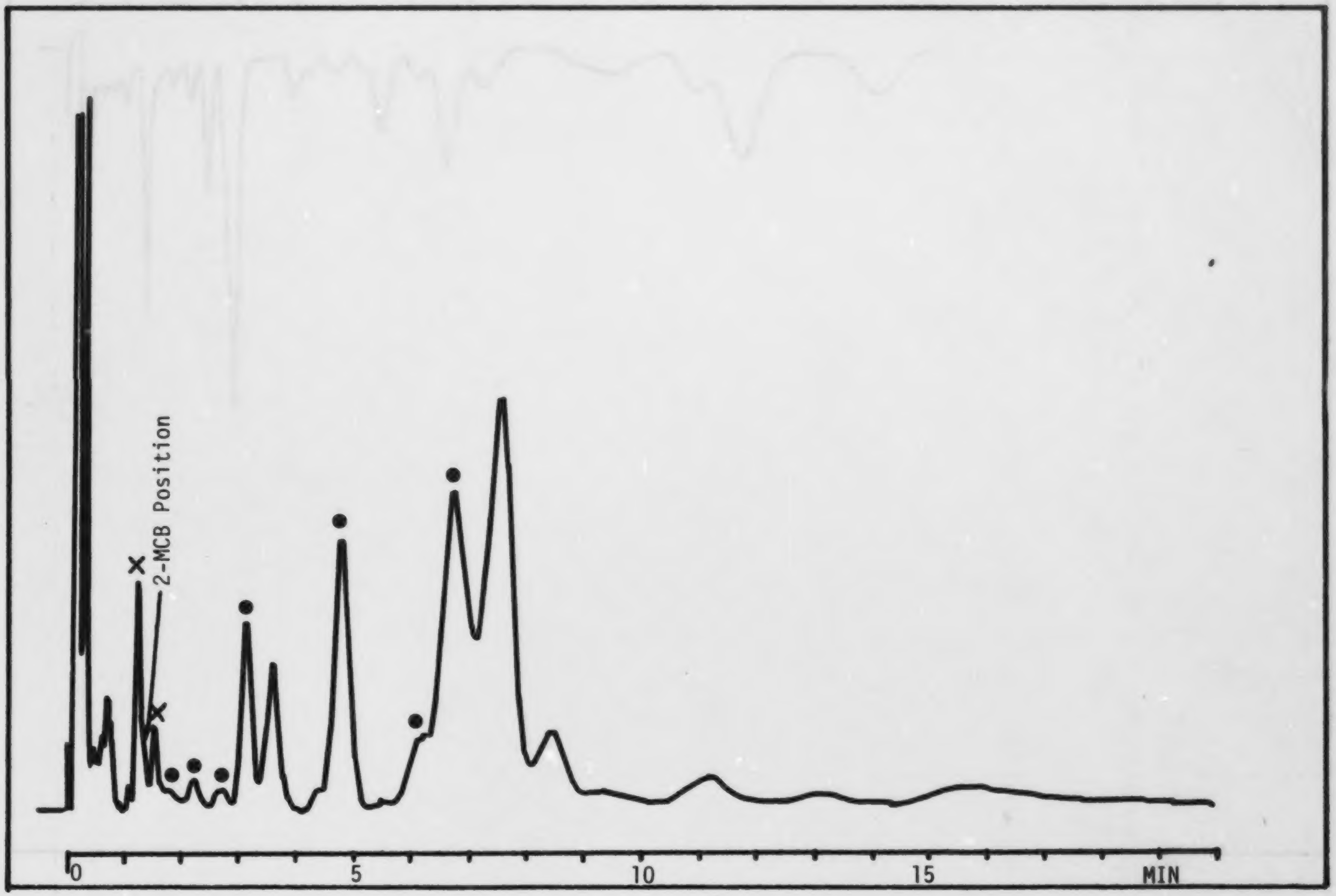


Figure 8(a). Chromatogram of an urban air sample, first polyurethane foam plug on SE-30/OV-210 column.

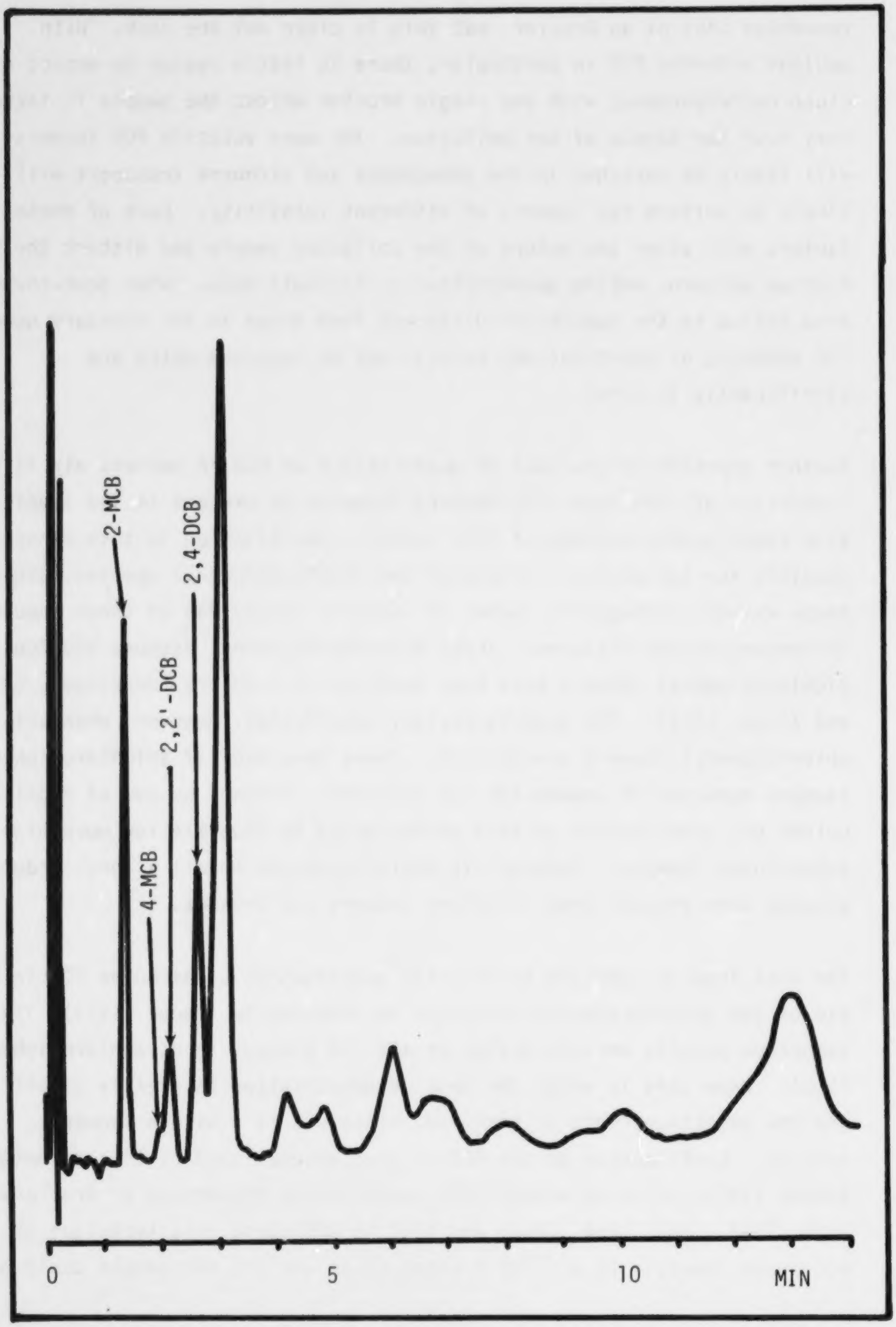


Figure 8(b). Chromatogram of Aroclor 1221 on SE-30/OV-210 column.

resembles that of an Aroclor, but this is often not the case. With ambient airborne PCB in particular, there is little reason to expect a close correspondence with any single Aroclor unless the sample is taken very near the source of the pollution. The more volatile PCB isomers will likely be enriched in the atmosphere and airborne transport will not likely be uniform for isomers of different volatility. Each of these factors will alter the nature of the collected sample and distort the GC elution pattern, making quantitation a difficult task. When peak-to-peak area ratios in the sample are different from those in the standard used for purposes of quantitation, results may be reported which are significantly in error.

Another approach to the task of quantitation of PCB in ambient air is by comparison of individual PCB isomers found to be present in the sample with known concentrations of that isomer. Quantitation in this manner is possible for the monochlorobiphenyl and dichlorobiphenyl species, since there exists a manageable number of isomeric variations of these species in commercial PCB mixtures. Three monochlorobiphenyl isomers and four dichlorobiphenyl isomers have been detected in Aroclors (Hutzinger, Safe, and Zitko, 1974). The task is rapidly complicated, however, when trichlorobiphenyl isomers are present. There have been 17 trichlorobiphenyl isomers detected in commercial PCB mixtures. Perhaps by use of capillary column GC, quantitation in this manner would be feasible for more highly substituted isomers. However, it would certainly entail a long, arduous process when greater than trichloro isomers are present.

The most logical approach to accurate quantitation of airborne PCB is by use of the perchlorination technique recommended by Armour (1973). This technique permits derivitization of all PCB present to decachlorobiphenyl (DCB). When this is done, the task of quantitation is greatly simplified and the detection limit is improved, since DCB is a single isomeric species. Confirmation of the PCB is also accomplished by this technique. Armour (1973) achieved essentially quantitative conversion of Aroclors 1016, 1242, 1248, 1254, 1260, and 1262 to DCB using this technique at microgram levels. If all PCB present in an ambient air sample could be chemically derivatized to DCB in this manner, quantitation would be accurate, precise, and reproducible from one analyst to the next with little variability due to subjective GC pattern interpretation. The nature of the PCB present can be qualitatively assessed before perchlorination.

Investigations were conducted into the use of the perchlorination technique for the analysis of ambient air samples for PCB collected on polyurethane foam. The method of Armour (1973) was initially used. The utility of this procedure is demonstrated by Figures 7(a) and 9. Figure 9 is a chromatogram of the same air sample shown in Figure 7(a) after perchlorination. Quantitation of PCB is obviously greatly simplified. The PCB is clearly separated in elution time from other materials which are not removed by the extensive cleanup procedures applied to the sample. The analytical detection limit is also greatly enhanced by perchlorination since the electron capture detector is much more responsive to DCB than lower-substituted isomers. The first polyurethane foam plug, shown in Figures 7(a) and 9, contained 1,790 ng of PCB as DCB; the second, 920 ng. The concentration on the third plug was equivalent to blank values observed for unexposed plugs.

Two problems in application of the Armour method had to be overcome, however, to achieve satisfactory results for airborne PCB. First, the method did not yield quantitative results when attempts were made to perchlorinate PCB species of less than trichloro substitution. Secondly, even for Aroclors, quantitative recovery was not achieved for less than 1 ug quantities of PCB. Both of these problems, it was discovered, were the result of the volatile loss of PCB during one step in the procedure where the extract is evaporated to near dryness. Furthermore, the recommended reaction temperature appeared to be sufficiently high to result in decomposition of the lower-substituted PCB species. After rather extensive experimentation and several modifications to the original Armour method, quantitative recovery was achieved for even the most volatile PCB species in sub-microgram quantities.

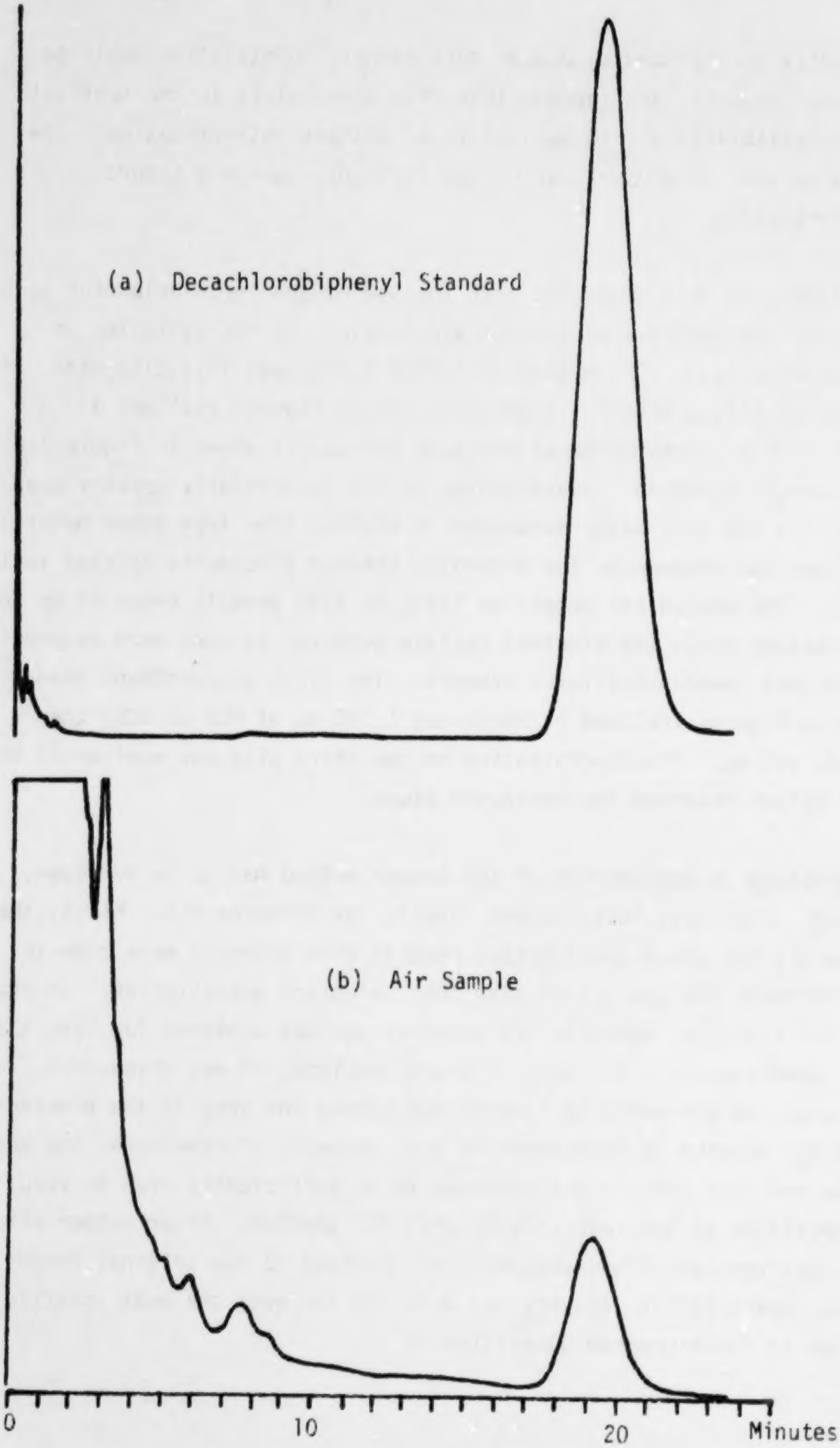


Figure 9. Chromatogram of a Perchlorinated Air Sample.

The sample is extracted from the polyurethane foam with hexane, concentrated, and cleaned up using silica gel. Since the perchlorination reaction cannot be carried out in hexane, all residual hexane must be removed from the extract prior to perchlorination. Even small amounts of residual hexane will result in the formation of a black, solid residue upon the addition of the antimony pentachloride ($SbCl_5$). This severely reduces PCB recovery. Attempts to remove the hexane by direct evaporation, even when very carefully conducted, invariably resulted in the volatile loss of dichlorobiphenyl and monochlorobiphenyl from test solutions. The hexane is, therefore, removed by azeotropic evaporation from a hexane/chloroform mixture. To the 1.0 ml extract in a Kuderna-Danish (K-D) apparatus, is added 10 ml of chloroform. This is concentrated by slow boiling to 4 ml. Repeat this azeotropic evaporation three additional times by adding 10 ml increments of fresh chloroform in order to remove all traces of hexane.

After removal of hexane, the chloroform extract is quantitatively transferred to a reaction vial, prepared as shown in Figure 10, using three chloroform rinses. The reaction vial is a 16 x 100 mm glass screw top culture tube with teflon-lined screw cap which has been modified by drawing the bottom into a cone shape. Reaction vials prepared in this manner were found to be easier to work with and much more reasonable in cost than the vacuum hydrolysis tubes recommended by Armour. The tapered bottom of the vial allows the analyst to reduce solvent volume to 0.1 ml without going to dryness. Add two boiling chips and immerse the reaction vial upright in a 70°C water bath to a depth of 6 $\pm$ 2 cm. Increase the water bath temperature slowly until the solvent begins to boil at 72-76°C. Concentrate slowly to a volume of approximately 0.1 ml. Under no circumstances should the water bath temperature be permitted to exceed 76°C nor should the solvent be evaporated to dryness. If either of these occurs, PCB will be lost by volatilization and consequent recoveries will be low. The final volume (0.1 ml) may be determined with sufficient accuracy by comparison of the solvent remaining with another reaction vial containing 0.1 ml of chloroform. Cap the reaction vial immediately after concentration and allow to cool.

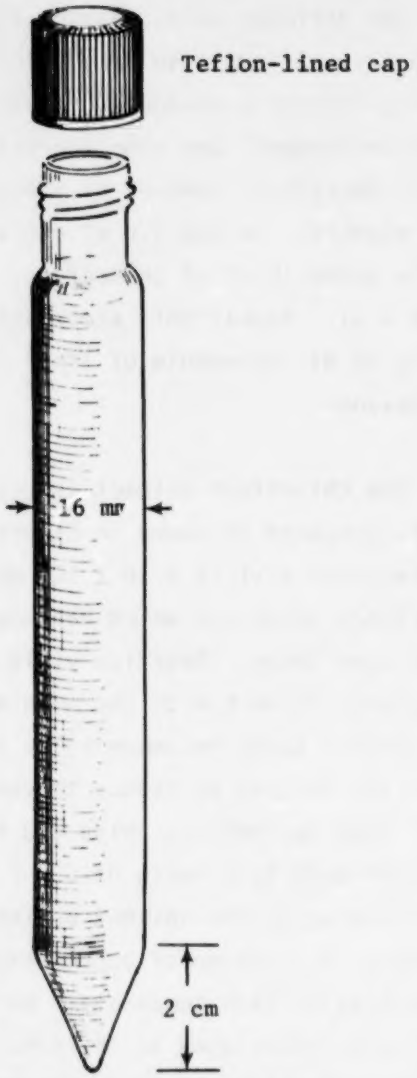

Teflon-lined cap
16 mm
2 cm

Figure 10. Perchlorination reaction vial.

Reagent grade $SbCl_5$ from several commercial sources has been found to contain DCB and bromononachlorobiphenyl (BNCB), as reported by Trotter and Young (1975). The DCB contaminant results in a positive blank value, and the BNCB interferes with the perchlorination of the lower-substituted PCB species. The $SbCl_5$ selected for use must first be analyzed for these contaminants. $SbCl_5$ manufactured by Cerac Pure (Stock Number A1147, Lot Number 15-26A) was found to be suitable. DCB contamination of this reagent is approximately 10 ng/ml. BNCB was not detected.

The reaction vial containing the sample is placed into a preheated ($160 \pm 3°C$) aluminum block heater for a period of 15 hours. It was found that the use of higher reaction temperatures (185°C) as recommended by Armour resulted in poor recovery of di- and mono-substituted PCB species. Apparently these species were not stable at the higher temperatures. Reaction temperatures less than 150°C also resulted in poor recovery due to incomplete conversion of lower-substituted PCB species to DCB. Shorter reaction periods may be adequate to affect quantitative derivatization; however, the 15-hour period is convenient for overnight, unattended use.

After the reaction period, the reaction vial is removed from the heater and allowed to cool to room temperature. Then it is cooled in an ice bath before the addition of 1 ml of 6 $\underline{N}$ HCl to inactivate the excess perchlorination reagent. Pressure from the reaction vial is cautiously vented in a fume hood, directed away from the analyst, to avoid any possibility of injury.

To extract the DCB from the reaction mixture, add 1 ml of hexane to the reaction vial, shake vigorously for 30 seconds, and carefully draw off the hexane layer with a disposable pipet. Place this hexane extract on the top of a 6 mm x 12 cm disposable pipet packed with 2 g of anhydrous Na_2SO_4. This column is prewashed with hexane. Repeat hexane extraction of the reactants in this manner five times. Tests have shown this repetition assures quantitative recovery of DCB. After passing all six increments of the hexane extract through the Na_2SO_4 column, pass two additional 1-ml portions of fresh hexane through the column. Collect all fractions in a 10-ml graduated K-D apparatus. Connect a modified micro-Snyder column to the K-D apparatus, add a single boiling chip, and evaporate in a water bath (70°C) to less than 0.5 ml. Add fresh hexane to bring the volume back to exactly 1.0 ml on the graduated K-D receiver. Cap the receiver tightly or transfer the contents to a sealed container to avoid evaporation of solvent prior to gas chromatographic analysis. Store in a cold, dark location to avoid any possibility of photodegradation.

It is recognized that biphenyl, if present in a sample extract, would perchlorinate to DCB. Therefore, attempts were made to remove biphenyl from the extract before the addition of the perchlorinating reagent. Two approaches were taken without success. First, it was attempted to selectively remove biphenyl from the reaction mixture by either hydrolysis or nitrification. H_2SO_4 and H_2SO_4/FSO_3H treatment of a mixture of biphenyl and PCB resulted in no effect. The use of concentrated FSO_3H and SO_2/H_2SO_4 each resulted in decomposition of both biphenyl and PCB. HNO_3/H_2SO_4 caused nitration of PCB and biphenyl. The use of an activated alumina chromatographic column to selectively isolate biphenyl from a PCB mixture was also evaluated. This method showed some promise; however, a considerable amount of research would have been required to find the most suitable conditions (e.g., column dimensions, eluting solvents, activity grade, etc.) for effective isolation of biphenyl. Therefore, it was decided not to pursue this technique further, but to develop GC conditions for the analysis of biphenyl.

The GC conditions using a flame ionization detector that are described in Appendix A (Section 12.0) were found to provide an adequate detection limit for biphenyl in a sample extract. Hence, if the analyst suspects biphenyl may be present, the GC/FID analysis is conducted to determine the amount present in the sample extract. The efficiency of conversion of biphenyl to DCB using the method described in Appendix A is 43.3 ± 8.8 percent. This conversion efficiency is based on ten replicate analyses at 3.4 ug and 0.7 ug biphenyl. The analyst may correct the results obtained upon perchlorination by subtracting that amount resulting from the conversion of biphenyl present in the extract to DCB. Biphenyl was detected during preliminary field tests near a transformer storage facility. Field tests at other locations did not yield detectable levels of biphenyl.

After the modifications described above were incorporated into the perchlorination method to eliminate the problems encountered with volatile loss of PCB and thermal decomposition of the lower-substituted PCB species, a series of method recovery studies were conducted. The modified perchlorination method, as described in detail in Appendix A, was tested using Aroclor 1016, Aroclor 1254, and a test mixture of the most volatile and least thermally stable PCB species. The test mixture consisted of 25 percent monochlorobiphenyl (2-MCB), 55 percent dichlorobiphenyl (2,2'-DiCB, 2,4-DiCB, 2,4'-DiCB), and 20 percent trichlorobiphenyl (2,2',5-TCB). The results of these recovery studies are summarized in Table 1. Quantitative recovery was achieved for even the most volatile species over the range of at least 100 ng to 10 ug concentration. The overall mean recovery for all tests was 100±5 percent. The difficulties with poor recovery of the lower-substituted species at sub-microgram concentrations have, therefore, been overcome by the modifications to the original procedure.

2.3.8 Perchlorination Ruggedness Test

A ruggedness test (Youden and Steiner, 1975) was performed on the final modified perchlorination method to assess the likelihood of achieving comparable interlaboratory results for PCB at low concentrations. The

TABLE 1

PERCHLORINATION RECOVERY VS. CONCENTRATION TEST RESULTS

PCB	PCB Concentration (ug)	Number of Replicates	Percent Recovery	Standard Deviation
Aroclor 1016	10.0	3	103	3.7
Aroclor 1016	5.0	3	105	2.1
Aroclor 1254	3.0	1	113	--
Test Mixture*	1.18	3	98	6.5
Aroclor 1016	0.750	4	93	5.6
Test Mixture*	0.412	2	101	1.1
Test Mixture*	0.103	3	101	4.7

* Consisting of 25% monochlorobiphenyl, 55% dichlorobiphenyl, and 20% trichlorobiphenyl.

statistical theory underlying the ruggedness testing methodology is discussed by Youden and Steiner (1975). Seven parameters are chosen for testing and their nominal values (the value specified in the procedure) are denoted by A, B, C, D, E, F, and G.

A challenging value for each of those parameters is then selected and denoted by a, b, c, d, e, f, and g. The challenging parameters should represent differences that might be introduced as a result of different analysts at different laboratories following the same procedure. A series of eight experiments are then conducted using the combinations of conditions specified in Table 2. Each of the eight experiments, which may be performed in replicate, produces a result. The experimental results are denoted as S, T, U, V, W, X, Y, and Z. The results can be grouped as follows, for example, to determine the difference attributable to variable A:

$$A\text{-}a = \frac{S + T + U + V}{4} - \frac{W + X + Y + Z}{4}$$

TABLE 2

EIGHT COMBINATIONS OF SEVEN FACTORS USED TO TEST THE RUGGEDNESS OF AN ANALYTICAL METHOD

Factor Value	Determination Number							
	1	2	3	4	5	6	7	8
A or a	A	A	A	A	a	a	a	a
B or b	B	B	b	b	B	B	b	b
C or c	C	c	C	c	C	c	C	c
D or d	D	D	d	d	d	d	D	D
E or e	E	e	E	e	E	e	E	e
F or f	F	f	f	F	F	f	f	F
G or g	G	g	g	G	g	G	G	g
Observed Result	S	T	U	V	W	X	Y	Z

After Youden and Steiner (1975).

The ruggedness test of the perchlorination method incorporated the seven factors listed in Table 3. These factors varied from nominal (procedure specified) conditions to the degree that might be expected of a competent analyst following the written procedure. The ruggedness test format and data are shown in Table 4. Each determination number consisted of triplicate analysis of a PCB test mixture containing 25 percent monochlorobiphenyl, 55 percent dichlorobiphenyl (three isomers) and 20 percent trichlorobiphenyl at a total concentration of 0.824 ug PCB. The test involved 24 separate analyses and, hence, has statistical reliability.

The ruggedness test results are tabulated in Table 5. All factors showed a difference of less than that of the blank. Hence, the challenging conditions that were applied in no way affected the outcome of the determination. Furthermore, the difference observed for the blank (no variation) determination was +3.25 percent, which is satisfactorily low. An estimate may be made of the analytical standard deviation as follows:

$$\text{standard deviation} = \sqrt{2/7\ D_i{}^2}$$

where D_i is the difference (Table 5) measured for each factor. When the data from Table 5 are entered into this formula, an estimated analytical standard deviation of 3.0 percent results. This is an acceptable level of variance for gas chromatographic analytical procedures.

TABLE 3

PERCHLORINATION RUGGEDNESS TEST CONDITIONS

Factor	Procedure Step No.*	Nominal	Challenging
Extract transfer rinse volume	8.2.3	A = 4 ml	a = 1 ml
Reaction temperature	11.4.2	B = 160°C	b = 165°C
$SbCl_5$ reagent volume	11.4.1	C = 0.2 ml	c = 0.1 ml
Final extract volume	11.3.6	D = 0.1 ml	d = 0.3 ml
Blank	--	E = e	e = E
Solvent evaporation temperature	11.3.5	F = 72°C	f = 76°C
Water bath immersion depth	11.3.4	G = 4 cm	g = 9 cm

*As described in Appendix A.

TABLE 4

PERCHLORINATION RUGGEDNESS TEST FORMAT AND DATA

Factor Value	Determination Number							
	1	2	3	4	5	6	7	8
Extract Transfer Rinse Volume A = 4.0 ml a = 1.0 ml	4.0 ml	4.0	4.0	4.0	1.0	1.0	1.0	1.0
Reaction Temperature B = 160°C b = 165°C	160°C	160	165	165	160	160	165	165
$SbCl_5$ Reagent Volume C = 0.2 ml c = 0.1 ml	0.2 ml	0.1	0.2	0.1	0.2	0.1	0.2	0.1
Final Extract Volume D = 0.1 ml d = 0.3 ml	0.1 ml	0.1	0.3	0.3	0.3	0.3	0.1	0.1
Blank E = e no variation	--	--	--	--	--	--	--	--
Solvent Evaporation Temperature F = 72°C f = 76°C	72°C	76	76	72	72	76	76	72
Water Bath Immersion Depth G = 4 cm g = 9 cm	4 cm	9	9	4	9	4	4	9
Observed Result	S	T	U	V	W	X	Y	Z
Observed Percent Recovery (%)	98.7	99.7	95.8	93.9	94.6	99.5	91.9	99.1
Observed Standard Deviation (%)	8.9	4.1	3.2	4.2	--	4.4	0.6	3.5

TABLE 5

PERCHLORINATION RUGGEDNESS TEST RESULTS

Rank	Factor	Difference (%)
1	Blank	+3.25
2	Reaction Temperature	+2.95
3	$SbCl_5$ Volume	-2.80
4	Final Extract Volume	1.40
5	Water Bath Immersion Depth	-1.30
6	Extract Transfer Method	0.75
7	Solvent Evaporation Temperature	0.15

The results of ruggedness testing of the modified perchlorination method indicate the method is "rugged" and therefore immune to modest departures from habitual routine on the part of the analyst. Furthermore, all method variables are in control. Variation within the specified limits of the procedure should not affect the outcome of the analysis. Competent trace analytical chemists following the above procedure in different laboratories should therefore achieve comparable analytical results.

3.0 RECOVERY STUDIES AND FIELD TESTS

After development of suitable laboratory analytical techniques and demonstration that these techniques permitted quantitative recovery of PCB ranging from mixtures of low substitution (e.g., Aroclor 1221) to mixtures of a high degree of substitution (e.g., Aroclor 1260), and after improvement of the perchlorination method, efforts were turned to an evaluation of the selected sampling method for airborne PCB. This evaluation was conducted in such a manner that it was, in fact, an evaluation of the entire method, including both sample collection and laboratory analysis. This chapter describes the results of collection efficiency and recovery studies of the method, preliminary field tests, and field tests of the final sampling and analytical method. The collection efficiency and recovery studies were conducted to identify the capabilities and limitations of the high-volume sampling method selected. The preliminary field tests described below were conducted over the course of development of the method. They provided valuable information pertinent to development of the method for routine use. Finally, after method development was complete and the method tested in the laboratory, it was subjected to several thoroughgoing field tests.

3.1 RECOVERY STUDIES

PCB recovery studies were first conducted with Aroclor 1221 and, more extensively, with Aroclor 1016. These two commercial mixtures were selected for the initial studies for two reasons. First, they are composed principally of the lower-substituted PCB species which are generally the more volatile ones. Secondly, Aroclor 1221 and Aroclor 1016 are commonly used commercial products.

It would be anticipated, and has been shown by Mieure (1975), that the more volatile PCB species are likely to be found in the atmosphere in greater amounts than the less volatile species. The molecular composition of several Aroclors is tabulated in Table 6. Aroclor 1221 is composed predominantly of biphenyl, monochlorobiphenyl, and dichlorobiphenyl.

TABLE 6

MOLECULAR COMPOSITION OF SOME AROCLORS (AFTER HUTZINGER, SAFE, AND ZITKO, 1974)

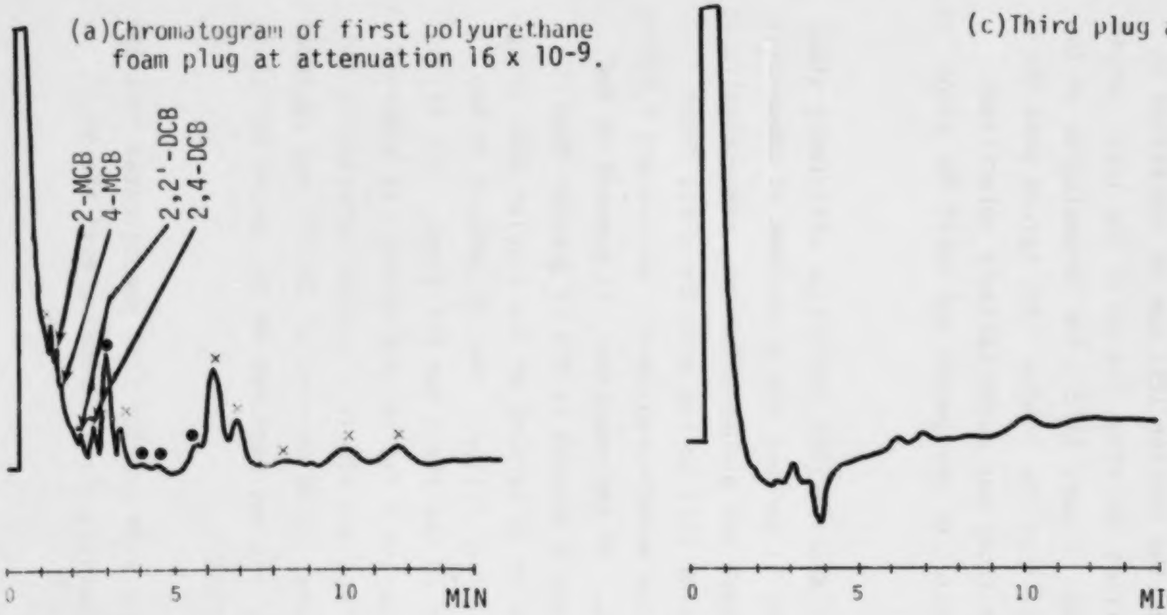
Chlorobiphenyl Composition	Presence in Aroclor (W/W%)			
	1221	1016	1242	1254
$C_{12}H_{10}$	11	<0.1	<0.1	<0.1
$C_{12}H_9Cl$	51	1	1	<0.1
$C_{12}H_8Cl_2$	32	20	16	0.5
$C_{12}H_7Cl_3$	4	57	49	1
$C_{12}H_6Cl_4$	2	21	25	21
$C_{12}H_5Cl_5$	<0.5	1	8	48
$C_{12}H_4Cl_6$	ND	<0.1	1	23
$C_{12}H_3Cl_7$	ND	ND	<0.1	6
$C_{12}H_2Cl_8$	ND	ND	ND	ND

* ND indicates <0.01%, none detected.

Aroclor 1016 is largely trichlorobiphenyl with significant amounts of dichlorobiphenyl and tetrachlorobiphenyl. Approximately 48 percent of the total domestic production of PCB in 1975 consisted of Aroclor 1016. Another 25 percent consisted of the closely related product Aroclor 1242 (Monsanto Co., 1975). Aroclor 1221 production quantities were much lower, comprising less than 1 percent of total annual production in 1975; however, Aroclor 1221 was produced in considerably larger quantities during the years 1957 to 1974.

The sampling system used for the collection efficiency studies is identical to that described earlier and illustrated in Figure 1. A Gelman 20 x 25 cm glass filter (Type A) which has been heated to remove any PCB contaminant is placed in the stainless steel filter holder. Three pre-cleaned polyurethane foam (PUF) plugs are fitted into the throat of the sampler in the manner described in the method (Appendix A). A known quantity of Aroclor, dissolved in isooctane or hexane, is quantitatively transferred to the center of the filter using a volumetric pipet. The sampler is immediately turned on at an adjusted flow rate of 0.8 m^3/min and the sampling period is commenced. Samplers were run 20 minutes for each of these initial recovery studies. Approximately 16 cubic meters of air were drawn through the glass fiber filter and the three PUF plugs. The tests were conducted in the laboratory using large enough PCB spike concentrations and short enough sampling periods that background levels could initially be ignored in computation of spike recoveries.

Figure 11 illustrates the first, second, and third PUF plug extract chromatograms and a chromatogram of the glass fiber filter extract after a recovery experiment using Aroclor 1221. Note the recorder attenuation factors indicated for these chromatograms. The first PUF plug chromatogram is shown at a recorder attenuation of 16×10^{-9}, while the others are shown at attenuation 4×10^{-9}. Those peaks designated by a "●" have been identified as peaks matching those present in Aroclor 1221; those designated by an "x" are not present in Aroclor 1221. The labeled peaks have been specifically identified using pure isomers of



(a)Chromatogram of first polyurethane foam plug at attenuation 16 x 10^{-9}.

(c)Third plug at attenuation 4 x 10^{-9}.

(b)Second plug at attenuation 4 x 10^{-9}.

(d)Chromatogram of the glass fiber filter at the end of the study at attenuation 4 x 10^{-9}.

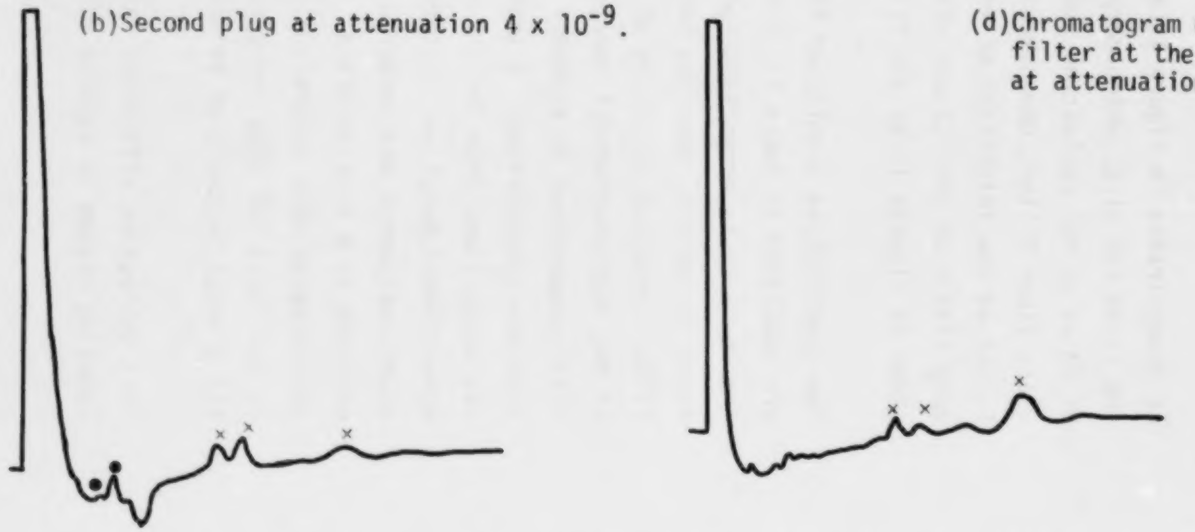


Figure 11. Chromatograms of the Aroclor 1221 collection efficiency study.

2-monochlorobiphenyl (2-MCB), 4-monochlorobiphenyl (4-MCB), 2,2'-dichlorobiphenyl (2,2'-DCB), and 2,4-dichlorobiphenyl (2,4-DCB). It was later determined that many of those peaks on the chromatograms which are designated by an "x" originated with the sampler exhaust. Recirculation from sampler exhaust to intake was apparently occurring. This problem was eliminated on subsequent work.

As demonstrated in Figure 11(a), the Aroclor 1221 can be identified on the first PUF plug, which comprises the first 7.6 cm of the total length of 23 cm of PUF collection media. Figure 11(d), the chromatogram of the glass fiber filter, demonstrates that the Aroclor 1221 spiked onto the filter at the initiation of the study was quantitatively volatilized. Very little of the PCB was detected on the second and third PUF plugs, as shown in Figures 11(b) and (c).

The quantitative results of the Aroclor 1221 collection efficiency study are tabulated in Table 7. Since 51 percent and 32 percent of commercial Aroclor 1221 is monochlorobiphenyl and dichlorobiphenyl, respectively, as shown in Table 6, then the Aroclor 1221 spiked onto the glass fiber filter contained 15,700 ng of the monochlorobiphenyl species and 9,840 ng of the dichlorobiphenyl species. Of the remainder, 11 percent of the total composition is biphenyl and 6 percent is PCB of greater than dichloro-substitution. A total of 98 percent of the Aroclor 1221 spike was volatilized from the glass fiber filter. Over 97 percent of the monochlorobiphenyl was captured on the first two PUF plugs. All of the dichlorobiphenyl was captured on the first two PUF plugs. If biphenyl is excluded from consideration, since the electron capture detector is not sensitive to this species, a total of 92 percent of the PCB was captured on the first PUF plug and 6 percent was captured on the second PUF plug, for a total recovery of 98 percent.

This collection efficiency study with Aroclor 1221 demonstrated that the sampling system is capable of quantitatively trapping even the most

TABLE 7

RESULTS OF AIRBORNE PCB COLLECTION EFFICIENCY STUDY USING AROCLOR 1221

30,750 ng of Aroclor 1221 spiked on high-volume filter. Sampler run 20 minutes, total of 16 m^3 air drawn.

	Monochlorobiphenyl ng (% of total)	Dichlorobiphenyl ng (% of total)	Total PCB* ng (% of total)
Spike	15,700	9,840	27,400
1st plug	13,600 (87%)	9,840 (100%)	25,300 (92%)
2nd plug	1,100 (7%)	500 (5%)	1,600 (6%)
3rd plug	500 (<3%)	<100 (<1%)	<600 (<2%)
Filter	550 (3%)	<100 (0%)	<650 (2%)

* Excluding biphenyl.

volatile PCB species present in commercial products. It also demonstrated the method, including both the sample collection and analysis, has the capability of accurate measurement of airborne PCB.

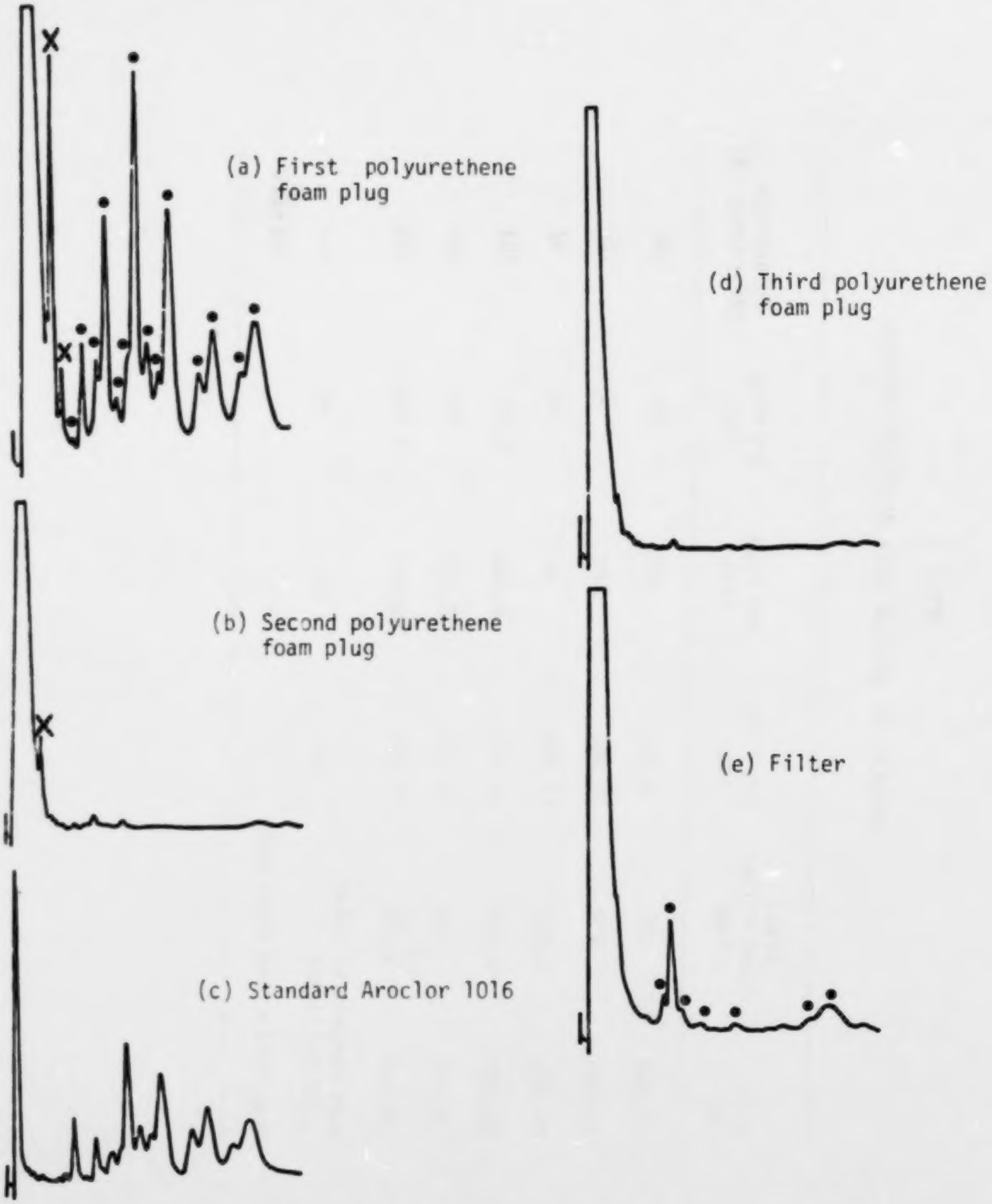
Six recovery studies were then conducted using Aroclor 1016. These were conducted in the same manner as the previously described recovery study. Spike concentrations covered the range of 5.6 to 120 ug of Aroclor 1016. Figure 12 is a series of typical chromatograms resulting from these studies. The one depicted is the 20 ug spike. The peaks indicated by a "●" match corresponding peaks in Aroclor 1016. The peaks designated by an "x" are the result of contaminants present in the laboratory atmosphere. They do not interfere with the Aroclor 1016 chromatogram. As can be seen by this figure, the PCB is quantitatively captured on the first PUF plug; that is, on the first 7.6 cm of PUF adsorbing media.

The quantitative results of all six studies are tabulated in Table 8. In general, over 95 percent of the Aroclor 1016 was volatilized from the glass fiber filter during each test. The collection efficiency shown in Table 8 is calculated as follows:

$$\text{Collection efficiency (\%)} = \frac{P_1+P_2+P_3}{S-F} \times 100;$$

where $P_{1,2,3}$ is the quantity of PCB found on the first, second, and third PUF plugs, respectively; S is the amount of PCB spiked onto the filter; and F is the PCB residue remaining on the filter at the conclusion of the experiment. The calculated collection efficiency, therefore, represents the recovery efficiency of the complete method, incorporating both the collection efficiency of the sampling device plus the analytical recovery of the laboratory procedure. The reported variance, likewise, encompasses both sampling and laboratory analysis.

A mean collection efficiency of 102 percent was achieved for Aroclor 1016 during this short-term collection study. The range was 89 to 117 percent and the standard deviation was 11 percent. This level of precision is



(a) First polyurethene foam plug

(b) Second polyurethene foam plug

(c) Standard Aroclor 1016

(d) Third polyurethene foam plug

(e) Filter

Figure 12. Aroclor 1016 recovery experiment.

TABLE 8

RESULTS OF AROCLOR 1016 RECOVERY STUDIES

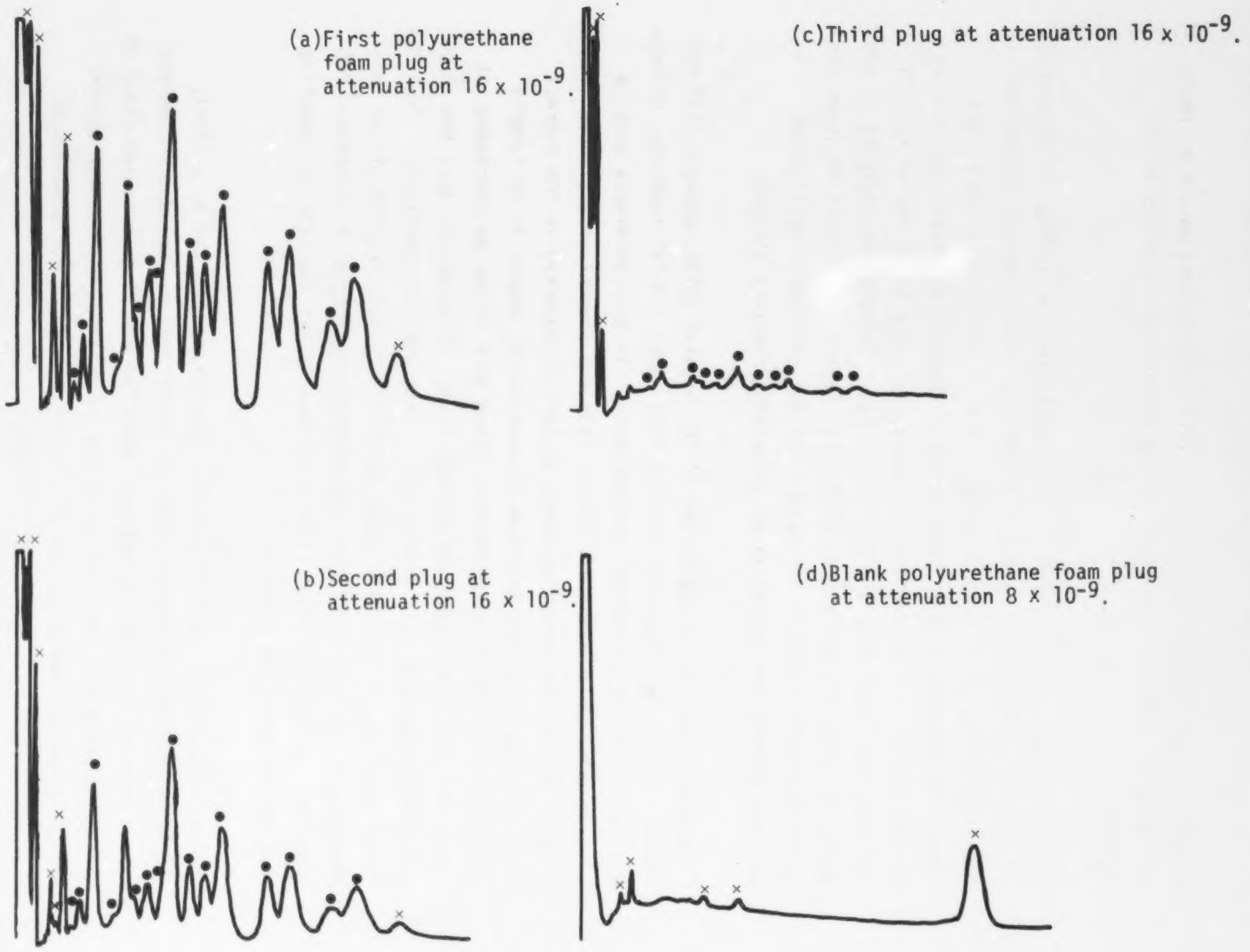
Spike (ng)	Glass Fiber Filter (ng)	1st Plug (ng)	2nd Plug (ng)	3rd Plug (ng)	Collection Efficiency (%)
5,600	190	3,400	760	650	89
11,200	610	12,300	120	0	117
20,000	1,380	17,060	80	40	92
28,000	1,030	21,570	4,050	2,180	103
56,000	890	52,020	2,230	760	100
112,000	3,290	77,690	38,800	3,010	110
Mean Percent of Total PCB Collected		85%	11%	4%	---
Mean Collection Efficiency					102±11%

acceptable for lengthy organic analysis techniques and should be representative of results achievable during routine applications of the method.

It is important to point out in these tests that an average of 85 percent of the PCB captured was retained on the first PUF plug and 96 percent was retained on the first two PUF plugs. Hence, three PUF plugs of the dimensions described above have proved sufficient to retain over 100 ug of airborne PCB. Furthermore, an average of only 4 percent of the PCB captured was located on the third PUF plug. Independent analysis of the third PUF plug extract would, therefore, permit the analyst to judge the collection efficiency of the system for the particular application desired without the necessity of conducting recovery studies.

Figure 13 shows the chromatograms of the highest spike recovery (112 ug) study. Again, "●" indicates Aroclor 1016 peaks and "x" indicates unidentified laboratory atmosphere contaminants. In this 20-minute test, a clearly detectable amount of Aroclor 1016 was present on all three PUF plugs. The entire chromatographic pattern is observed in the extract from each PUF plug, and the peak-to-peak ratios appear to be largely unchanged from one plug to another. From this it may be concluded, at least for very short sampling periods (e.g., 20 minutes), that the chromatographic pattern is a reflection of true ambient conditions. Over the short sampling period there seems to be little modification of the chromatographic pattern resulting from selected retention of individual PCB species. It will be shown later that this is not the case for sampling periods in excess of 6 hours.

These initial tests confirmed that polyurethane foam can be a highly efficient collection medium under the conditions recommended in the proposed high-volume sampling method. When two PUF plugs are used (15.2 cm of adsorbent media) over 100 ug of PCB is retained with a high degree of efficiency. The inclusion of a third section of PUF provides a



(a)First polyurethane foam plug at attenuation 16 x 10^{-9}.

(b)Second plug at attenuation 16 x 10^{-9}.

(c)Third plug at attenuation 16 x 10^{-9}.

(d)Blank polyurethane foam plug at attenuation 8 x 10^{-9}.

Figure 13. Chromatograms from an Aroclor 1016 collection efficiency study.

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safety factor and a mechanism of estimating the collection efficiency by independent analysis of the third PUF plug in the samples. All PCB species from mono-substituted to tetra-substituted are efficiently retained on the adsorbing medium. It is reasonable to expect penta-substituted through deca-substituted PCB would, likewise, be effectively captured from the atmosphere.

Further testing of collection efficiency and recovery at lower PCB concentrations and for longer sampling periods had to await improvement of the perchlorination method for PCB quantitation as described above, since no method was readily available for producing large volumes of PCB-free air to conduct the tests. It was apparent that unless the perchlorination method could be adapted for use, background levels of PCB and other substances collected in the sample would obscure the test results. It would be extremely difficult to discern a low-level Aroclor pattern and nearly impossible to accurately measure the amount present by pattern matching techniques. After improvement of the perchlorination method and demonstration that it worked effectively for the full range of PCB species, collection efficiency and recovery studies were conducted using a synthetic PCB test mixture, three single volatile PCB isomers, and Aroclor 1242.

The composition of the PCB test mixture is listed in Table 9. The test mixture was spiked onto the glass fiber filter immediately before the test began in the same manner as Aroclor 1221 described above. The test was run out-of-doors in Gainesville, Florida. Along with this and each succeeding test, a background sample was taken at the same location during the same period of time as the test spike sample. Background PCB concentrations determined by analysis of the background sample glass fiber filter and each of the three PUF plugs were subtracted from the respective analytical results of the test spike sample to determine spike recovery. The background samples are described in a later section.

TABLE 9

PCB TEST MIXTURE COMPOSITION

PCB	Concentration	Percent Composition
2-MCB	0.44 ug/ml	18.7%
2,4-DiCB	0.40 ug/ml	57.0%
2,4'-DiCB	0.52 ug/ml	
2,2'-DiCB	0.42 ug/ml	
2,2',5-TCB	0.57 ug/ml	24.3%

The results of a 1-hour test using the volatile PCB test mixture (2.59 ug spike) are tabulated in Table 10. These results are reported as DCB after perchlorination. The collection efficiency is 90 percent based on recovery of the spike. Of the total PCB collected on the PUF, 93 percent was captured on the first PUF plug. This test showed even the most volatile PCB species could be retained over a 60-minute period, and that satisfactory results could be achieved using the perchlorination technique.

In order to further define the behavior of the more volatile PCB species in the system, even longer-term collection efficiency tests were run using pure isomers of 2,2',5-TCB, 2,4'-DiCB, and 2-MCB. The results of these 2-hour (120 m^3) tests are tabulated in Table 11. TCB spike recovery averaged 91 ± 3 percent for two separate 0.48 ug spikes (1,115 ng as DCB). DiCB showed a 103 percent recovery for a 1.08 ug spike (2,080 ng as DCB). In the case of both TCB and DiCB, quantitative capture was achieved on the first PUF plug alone. MCB demonstrated a 107 percent collection efficiency. Unlike the other species, however, MCB penetrated beyond the first PUF plug to the second and the third PUF

TABLE 10

RESULTS OF INITIAL RECOVERY STUDY USING PCB TEST MIXTURE*

Sample Duration (min)	60
Flow Rate (m^3/min)	0.76
Volume Air Sampled (m^3)	46
Ambient Temperature (°C)	32.5
Ambient Humidity (%)	39
Spike Concentration (ng @ DCB)	2590
Background Corrected † PCB (ng DCB)	
Filter	373
PUF #1	1850
PUF #2	0
PUF #3	147
Total	2370
Percent of Total PCB Collected on PUF (%)	
PUF #1	93
PUF #2	0
PUF #3	7
Collection Efficiency (%)	90

* Test mixture composition shown in Table 9. Sample date 4/22/77.

† Background levels are described in Table 18.

TABLE 11

RESULTS OF 2-HOUR RECOVERY STUDIES USING TCB, DiCB, AND MCB

	TCB Spike*		DiCB Spike †	MCB Spike †
Sample Date	7/26/77	7/26/77	11/28/77	11/28/77
Sample Time	1250-1458	1250-1458	1553-1753	1553-1753
Sample Duration (min)	128	128	120	120
Flow Rate (m^3/min)	0.74	0.78	0.62	0.62
Volume Air Sampled (m^3)	95	100	75	75
Ambient Temperature (°C)	35.5	35.5	25	25
Ambient Humidity (%)	39	39	48	48
Spike Concentration	1115 ng @ DCB	1115 ng @ DCB	2080 ng DiCB	2290 ng MCB
Background Corrected PCB*				
Filter	48 ng DCB	2 ng DCB	0 ng DiCB	0 ng MCB
PUF #1	949	1034	2142	640
PUF #2	0	0	0	1340
PUF #3	0	0	0	490
Total	997	1036	2142	2470
Percent of Total PCB Collected on PUF (%)				
PUF #1	100	100	100	26
PUF #2	0	0	0	54
PUF #3	0	0	0	20
Collection Efficiency	89%	93%	103%	108%

---

* Background sample data may be found in Table 18. Quantitated by perchlorination. Spike 0.576 ug 2,2',5-TCB.

† Single peak quantitation for 2,4'-DiCB and 2-MCB.

plugs as indicated in Table 11. Twenty percent of the total MCB was captured on the third PUF plug and the greatest amount (54 percent) was detected on the second rather than the first PUF plug. Apparently, the more volatile MCB moves through the PUF at a significantly faster rate than either DiCB or TCB. The 2-hour sampling period is, therefore, about the maximum duration that can be used while achieving quantitative capture and retention of MCB, but is entirely suitable for the capture and retention of PCB species of higher substitution. Shorter sampling periods would be more suitable for the collection of MCB as demonstrated by the quantitative recovery achieved during the 20-minute test using Aroclor 1221 as described above.

A 12-hour test was then conducted using MCB, DiCB, and Aroclor 1242 to determine the maximum length of time that various PCBs could be expected to be retained on the PUF material. The results of this test are reported in Table 12. As expected, during this 12-hour sampling period in which 634 m^3 of air were drawn through the system, MCB was not effectively retained. A collection efficiency of only 4 percent was achieved for the 0.52 ug spike. All MCB residual was located on the second and third PUF plugs, with 64 percent of the total on the third plug. Ninety-three percent of the DiCB spike (2.08 ug) was captured during this test, but 28 percent was located on the third PUF plug, 53 percent on the second, and only 19 percent on the first. It is clear from this and the preceeding data for the 20-minute and 2-hour tests, that each PCB species moves through the PUF in a band much like it would move through a chromatographic column. The lower-substituted species (e.g., MCB, DiCB) move more rapidly through the system than the higher-substituted species (e.g., TCB). This will, therefore, limit the duration of sampling that can be employed.

Aroclor 1242 was effectively captured on the first PUF plug (Table 12) during a 12-hour test run using a 10.4 ug spike. Aroclor 1242 is reported (Table 6) to contain 1 percent MCB, 16 percent DiCB and the remainder TCB and more highly-substituted PCB species. Hence, only MCB limits the sampling duration to less than 12 hours.

TABLE 12

RESULTS OF 12-HOUR RECOVERY STUDIES USING AROCLOR 1242, MCB AND DiCB*

	Aroclor 1242 Spike Run †	DiCB Spike Run**	MCB Spike Run**
Flow Rate (m^3/min)	1.0	0.88	0.88
Vol. Air Sampled (m^3)	720	634	634
Spike Concentration	10,400 ng Aroclor 1242	2,080 ng DiCB	5,200 ng MCB
Background Corrected PCB			
PUF #1	12,064 ng Aroclor 1242	370 ng DiCB	0 ng MCB
PUF #2	NA	1,020	80
PUF #3	NA	550	140
Total	12,064	1,940	220
Percent of Total PCB Collected on PUF (%)			
PUF #1	100	19	0
PUF #2	NA	53	36
PUF #3	NA	28	64
Collection Efficiency (%)	116	93	4

NA = not analyzed.

* Test run during the period 0751-1951 (720 minutes) on 12/5/77. Ambient temperature 22°C. Ambient relative humidity 100% (heavy rainfall).

† Pattern matching quantitation.

**Single peak quantitation using 2,4-DiCB and 2-MCB.

A 6-hour recovery test using Aroclor 1242 was run in duplicate. The results of this test are tabulated in Table 13. The mean collection efficiency was 89 percent after background correction. Since relatively large spike concentrations (10.4 ug) were employed, quantitation of this test could be accomplished by pattern matching methods, as demonstrated in the following figures. In the case of both spike samples and the background sample, over 99 percent of the total PCB was captured on the first and second PUF plugs. The third plug in each case had little or no detectable PCB.

Figure 14 is the chromatogram of an Aroclor 1242 standard at the same GC conditions as the recovery sample shown in Figure 15(a), (b), and (c). Figure 15 (a) is the chromatogram of the first PUF plug showing a complete Aroclor 1242 pattern. Peaks matching those in the Aroclor 1242 standard are designated by a "●". In addition to the Aroclor 1242 that was captured, other earlier eluting compounds are evident. Two isomers of DDE (o, p'-DDE and p, p'-DDE) have apparently been captured from the ambient atmosphere on the first PUF plug, although these peaks have not been confirmed. The first PUF plug retained a total of 11.6 ug of Aroclor 1242, while the second and third PUF plugs retained 0.27 ug and 0.07 ug, respectively. The chromatograms for the second and third PUF plug extracts are shown in Figure 15(b) and (c), respectively. Only traces of PCB remained on the glass fiber filter. In order to determine the collection efficiency in this test, background PCB had to be subtracted from the filter and each PUF plug. Chromatograms of the background sample taken during this test are discussed in a later section (see Figures 25 and 26). After correction for the background residual PCB, the first PUF plug extract contained 9.08 ug Aroclor 1242 while the second and third PUF plug extracts contained background corrected concentrations of 0.17 ug and 0.07 ug Aroclor 1242, respectively.

A final series of recovery tests were conducted using Aroclor 1242 to determine if recovery was dependent on airborne PCB concentration. The results are tabulated in Table 14. Spike concentrations of 10.4 ug,

TABLE 13

RESULTS OF 6-HOUR RECOVERY STUDIES USING AROCLOR 1242

	Spike Run A †	Spike Run B †	Background ††
Sample Date*	11/20/77	11/20/77	11/20/77
Sample Time	1216-1815	1216-1815	1216-1815
Sample Duration	359	359	359
Flow Rate (m^3/min)	0.92	0.96	1.0
Vol. Air Sampled (m^3)	331	347	360
Spike Concentration (ng Aroclor 1242)	10,400	10,400	---
PCB Retained (ng Aroclor 1242)			
Filter	18	18	18
PUF #1	11,650	12,160	3,060
PUF #2	272	399	109
PUF #3	72	10	0
Total	12,010	12,590	3,190
Percent of Total PCB Collected on PUF (%)			
PUF #1	97	97	97
PUF #2	2	3	3
PUF #3	1	0	0
Background Corrected PCB (ng Aroclor 1242)			
Filter	0	0	
PUF #1	8,840	9,210	
PUF #2	172	294	
PUF #3	72	10	
Total	9,084	9,514	
Collection Efficiency (%)	87.3	91.5	
Mean	89.4%		

*Ambient temperature 26°C.

†Pattern matching quantitation. Chromatograms shown in Figure 15.

††Chromatograms shown in Figures 25 and 26.

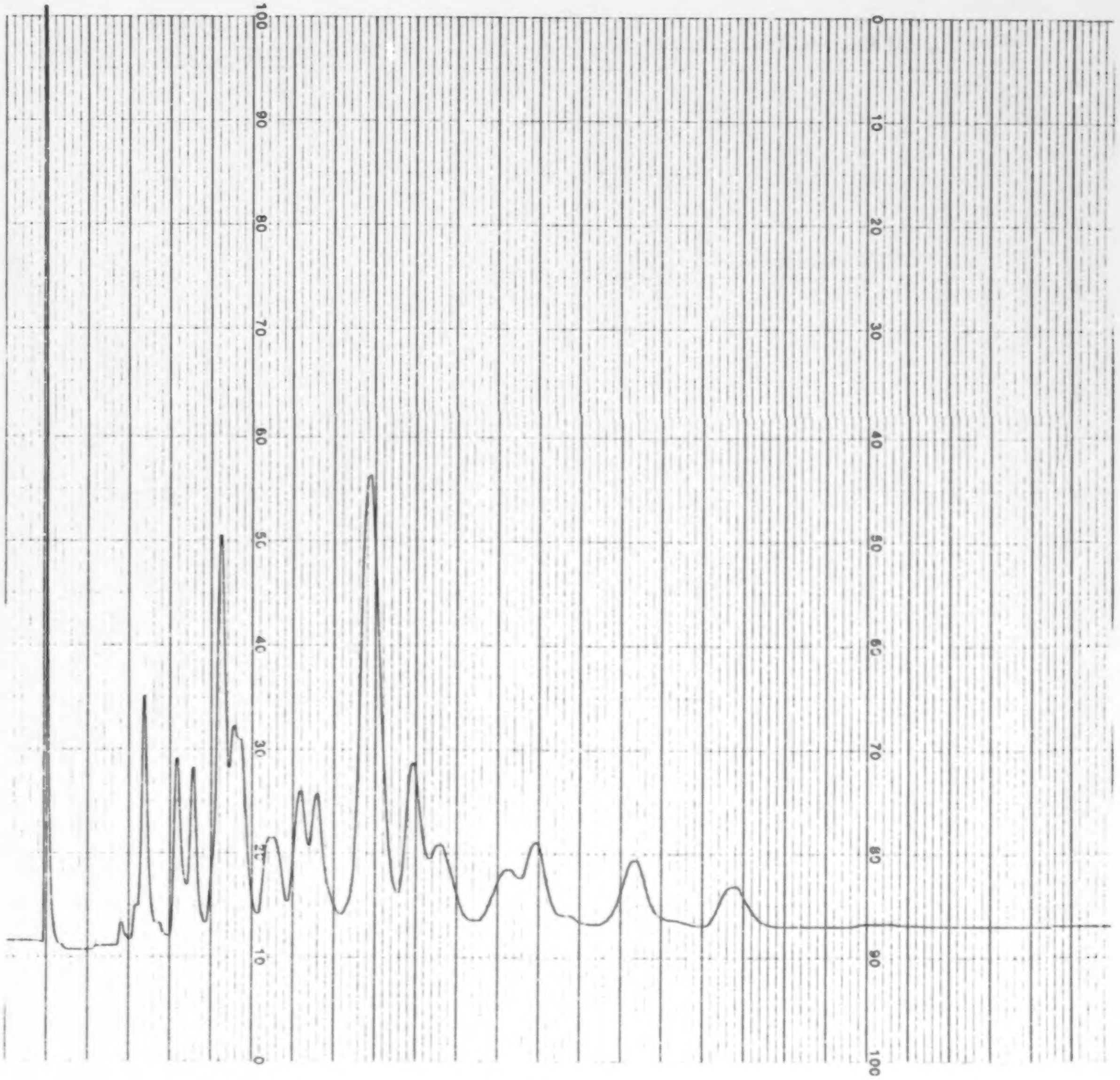

Figure 14. GC/EC Chromatogram of Aroclor 1242 Standard (Attn: $16x10^{-9}$).

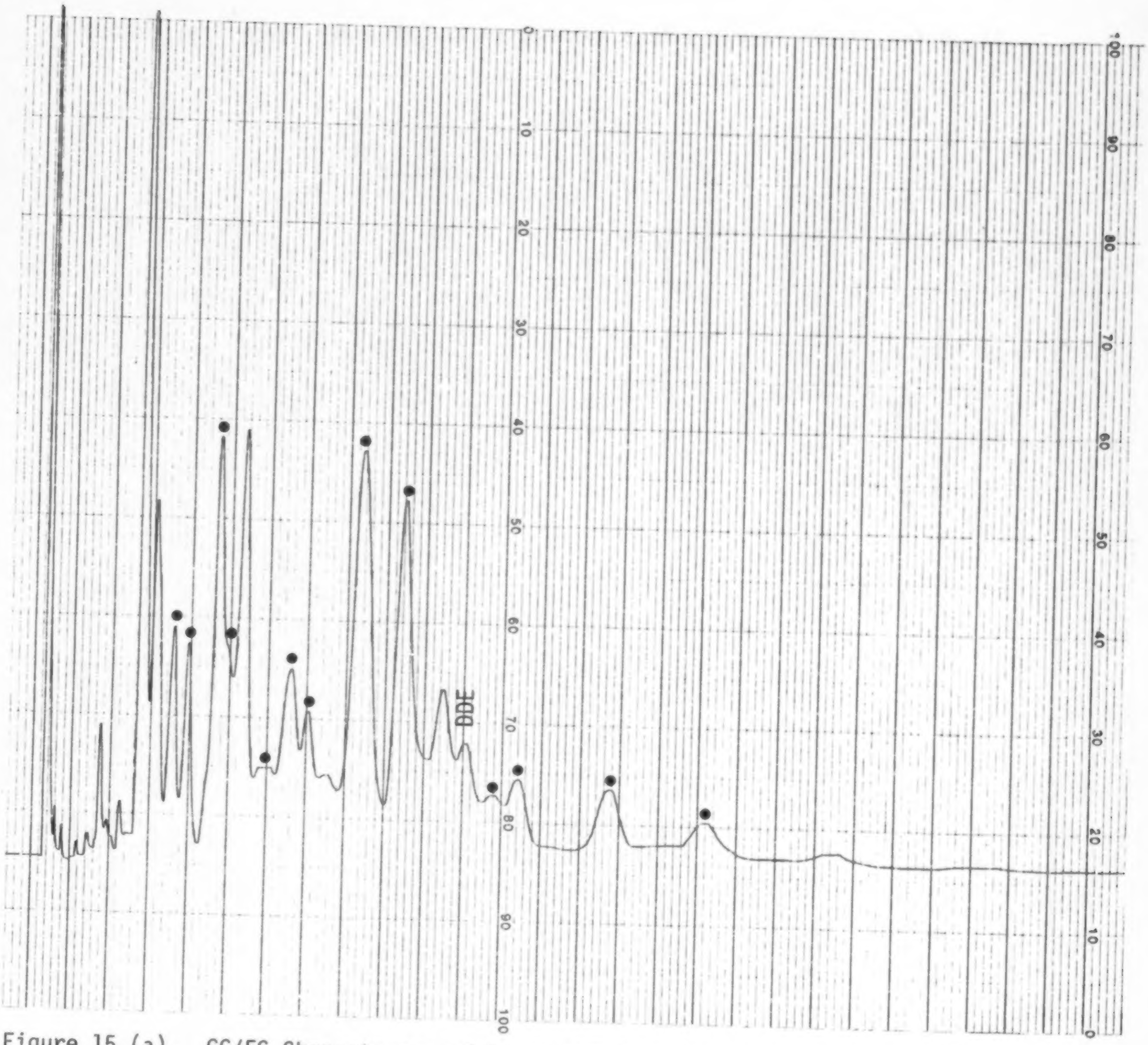

Figure 15 (a). GC/EC Chromatogram of First PUF Plug Extract (Attn: 16×10^{-9}) from 6-Hour Aroclor 1242 Recovery Study.

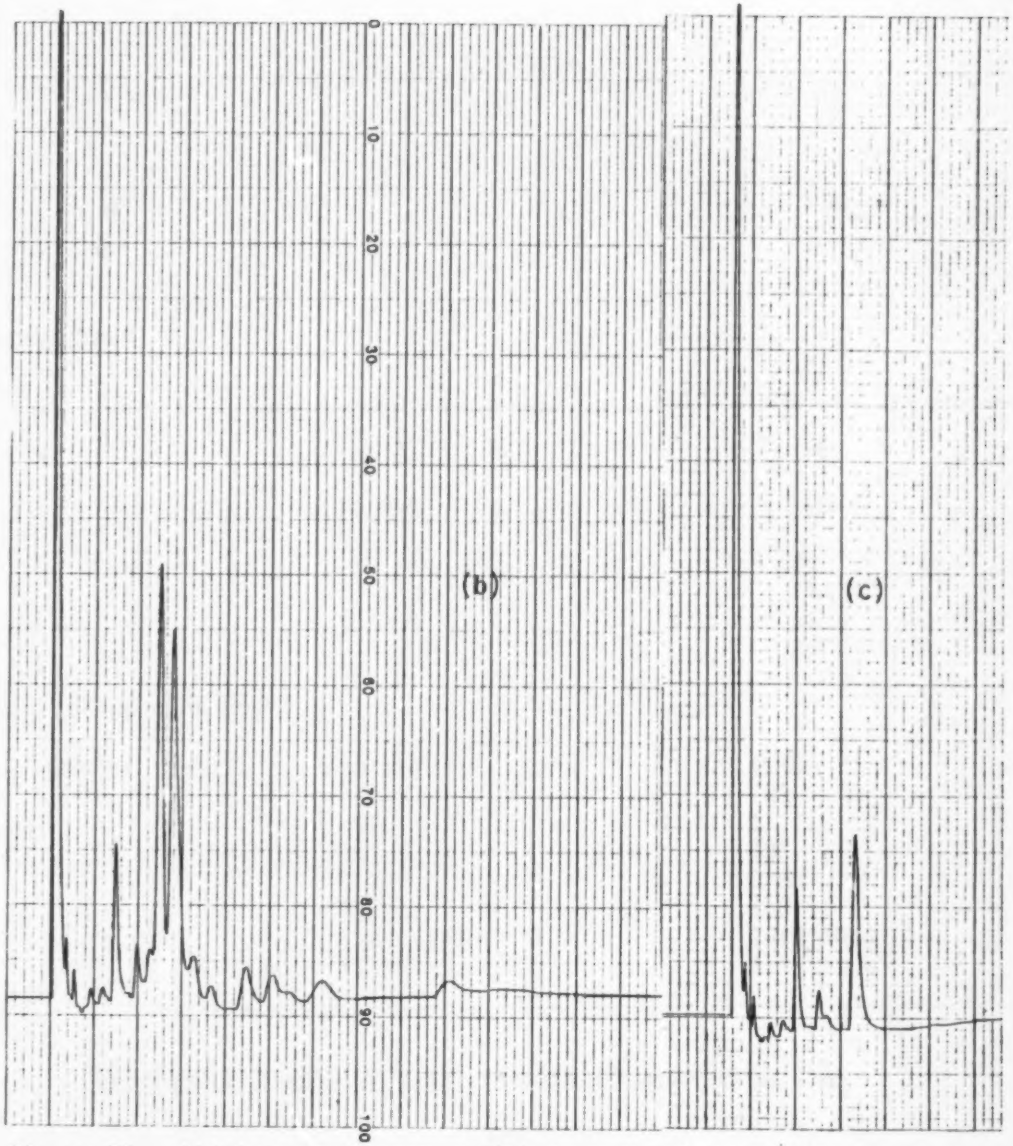

Figure 15. GC/EC Chromatogram of (b) Second and (c) Third PUF Plug Extracts (Attn: 16×10^{-9}) from 6-Hour Aroclor 1242 Recovery Study.

TABLE 14

RESULTS OF 2-HOUR RECOVERY STUDIES USING AROCLOR 1242

Sample Date*	11/28/77 †	12/8/77 †	12/8/77 †
Sample Time	1553-1753	1845-2045	1845-2045
Sample Duratjon (min	120	120	120
Flow Rate (m^3/min)	0.69	0.85	0.78
Vol. Air Sampled (m^3)	83	102	93
Ambient Temperature (°C)	25	11.6	11.6
Ambient Humidity (%)	48	83	83
Spike Concentration (ng Aroclor 1242)	10,400	4,970	1,130
Background Corrected PCB (ng Aroclor 1242)			
Filter	0	NA	NA
PUF #1	10,080	4,770	1,250
PUF #2	0	NA	NA
PUF #3	0	NA	NA
Total	10,080	4,770	1,250
Collection Efficiency (%)	97	96	111

NA = not analyzed
†Pattern matching quantitation.

5.0 ug, and 1.1 ug were used along with a 2-hour sampling period. Collection efficiencies were 97, 96, and 111 percent, respectively, for the three spike concentrations after subtraction of background levels. These values lie within the normal range of analytical variability for the method. Hence, there is no apparent interrelationship between recovery and concentration over the range tested.

The results of all the recovery tests that were conducted to validate the sampling and analytical method are summarized in Table 15. The following conclusions may be drawn from these studies:

a. There is no apparent variation in either collection efficiency or recovery as a result of variations in sample flow rate over the range of 0.6 to 1.0 m^3/min.

b. Ambient temperature and ambient humidity exerted no obvious influence on collection efficiency. One test was conducted during heavy rainfall with satisfactory results.

c. The pattern matching method of quantitation is reasonably accurate for the analysis of Aroclor concentrations in excess of 1 ug in the PUF extract. Perchlorination is required for lower concentrations. When the sample elution pattern does not closely resemble an Aroclor, the perclorination method should be routinely used to achieve accurate results.

d. The various PCB species move through the PUF collection medium much like they would move through a chromatographic column. Bleedthrough, or loss of PCB from the system, occurs in the order of MCB followed by DiCB and presumably by succeedingly higher-substituted species. If too long a sampling period is employed, lower-substituted PCB species, in particular MCB, will pass through the system undetected.

e. To assure quantitative (i.e., greater than 85 percent) collection efficiency for all PCB species, a sampling period of 2 hours should not be exceeded. If MCB is not a significant constituent of the

TABLE 15

SUMMARY OF RECOVERY TESTS

Species/Mixture Tested	No. Tests	Flow Rate (m^3/min)	Sample Time (min)	Vol. Air Sampled (m^3)	Collection Efficiency (%)	Total Collected on PUF#1 + PUF #2 (%)
Aroclor 1221	1	0.80	20	16	100	98
Aroclor 1016	6	0.80	20	16	102 ± 11	94 ± 9
Synthetic Test Mixture*	1	0.76	60	46	90	93
2,2',5-TCB	2	0.76	128	98	91 ± 3	100 ± 0
2,4-DiCB	1	0.62	120	75	103	100
2,4-DiCB	1	0.88	720	634	93	72
2-MCB	1	0.62	120	75	108	80
2-MCB	1	0.88	720	634	4	36
Aroclor 1242	1	1.0	720	720	116	100
Aroclor 1242	2	0.94	359	339	89 ± 3	100 ± 0.7
Aroclor 1242	3	0.69 - 0.85	120	83 - 102	101 ± 8	100

*Containing 19% MCB, 57% DiCB, and 24% TCB.

total airborne PCB present in the atmospheric sample, as was found to be the case in the field tests discussed later, then it is estimated from the recovery tests that up to a 6-hour sampling period can be accommodated with satisfactory recoveries. TCB and more highly-substituted species are retained for sampling periods in excess of 12 hours.

f. The mean collection efficiency for all the tests conducted for Aroclor 1016/1242 was 101 ± 10 percent with sampling periods ranging from 20 minutes to 12 hours.

g. When the duration of sampling is within the limits specified in 'e' above, independent assessment of the amount of PCB captured on the third PUF plug will allow the analyst to confirm a high collection efficiency for the airborne PCB without the necessity of conducting recovery tests.

3.2 PRELIMINARY FIELD TESTS

During the course of development of the recommended method presented in Appendix A, some preliminary field investigations were necessary. Certain aspects of these preliminary field data have been previously discussed in the appropriate section of this report. Brief mention will be made at this point of the findings from those preliminary investigations which have not been discussed in an earlier chapter.

Samples were taken of urban ambient atmosphere in Jacksonville, Florida, using a single polyurethane foam plug of the dimensions described in the method in each high-volume sampler. Collection efficiency is, therefore, not known, but it is expected to be less than the laboratory studies where three polyurethane foam plugs were used in each sampler. Several samples were collected periodically over a 24-hour period. Sample periods of 2 to 24 hours were selected. The volume of air sampled and the analytical results are shown in Figure 16. No PCB was detected in the glass fiber filters used in the sampling apparatus. These data are considered to represent minimum ambient airborne PCB concentrations.

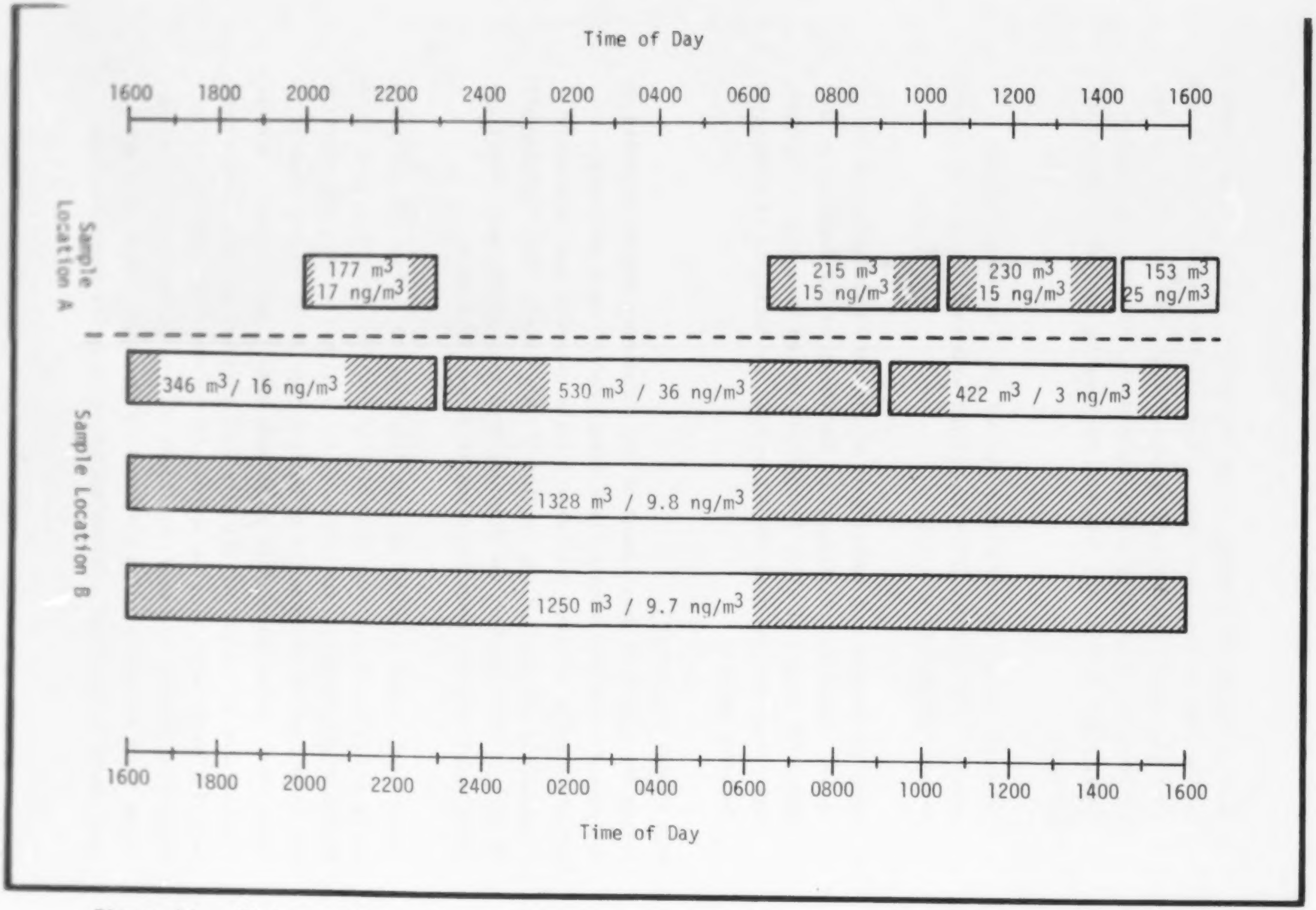

Figure 16. Minimum ambient airborne PCB concentrations in an urban environment.

Values observed ranged from 15 ng/m^3 to 25 ng/m^3 at sample location A and from 3 ng/m^3 to 36 ng/m^3 at sample location B. At sample location B, there appears to be a greater variability with time of day than at sample location A.

Figure 17 illustrates a typical chromatogram obtained during this test. There are numerous extraneous peaks on the chromatogram which make interpretation and quantitation difficult. At the time this sample was taken, precautions were not used to prevent sampler recirculation since the problem was not known. It appears that the PCB present falls in the range of Aroclors 1242 and 1254. A "●" indicates peaks that clearly match corresponding Aroclor peaks.

A second preliminary field evaluation was conducted at sample location B in Jacksonville. Three polyurethane foam plugs were used this time and the maximum sampling period was shortened to 6 hours. Unfortunately, all analytical results were less than the detection limit. Ambient levels were apparently significantly lower at this time.

A third sampling was conducted at this location to obtain additional field samples for evaluation. Samples were collected at 4-hour intervals over a 24-hour period. The results are tabulated in Table 16. A reasonably uniform PCB concentration was measured over the course of the 24-hour period. Concentrations varied from 4 ng/m^3 to 9 ng/m^3. The chromatograms obtained have been discussed in a previous chapter of this report.

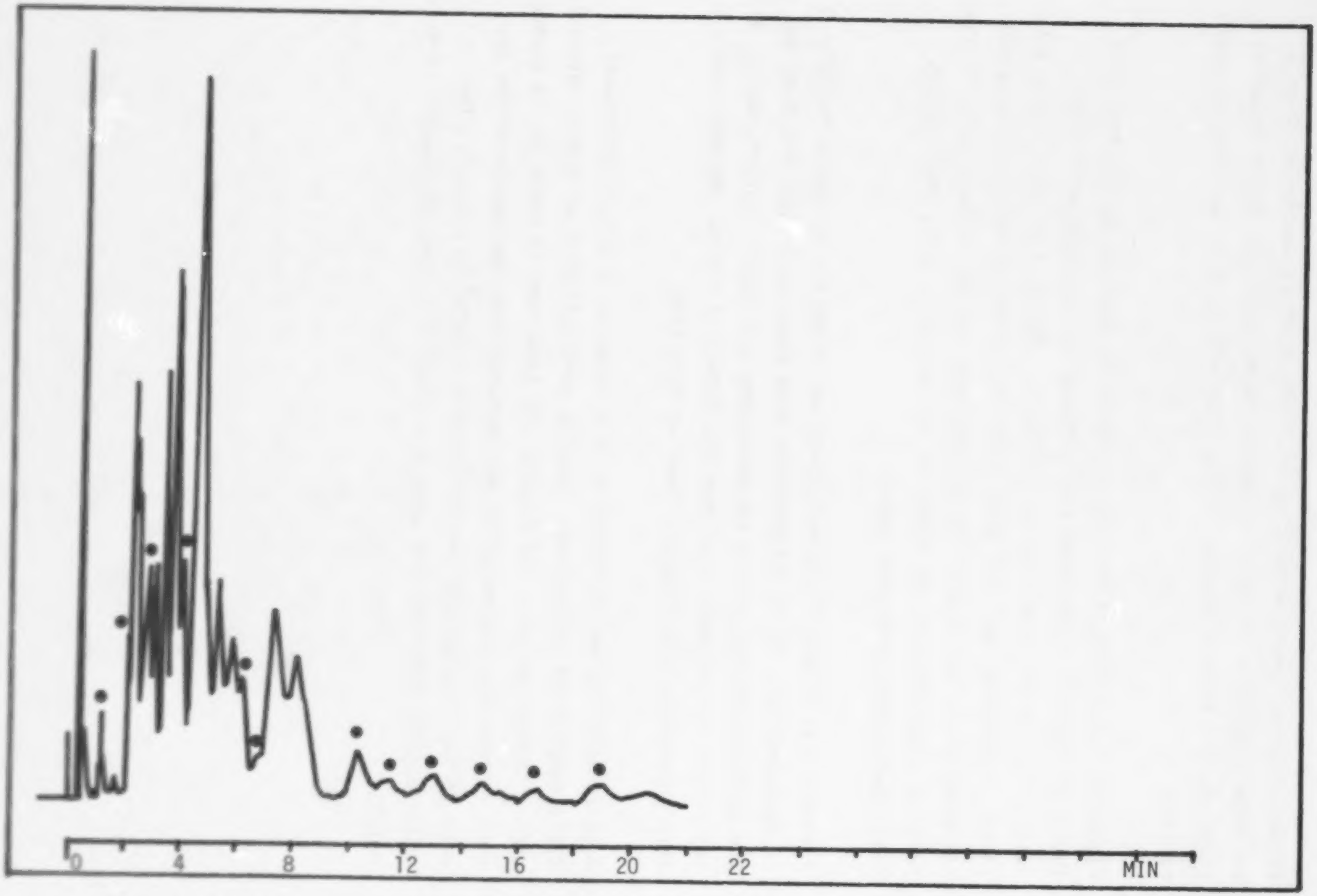

Figure 17. Chromatogram of an urban ambient air sample.

TABLE 16

PCB IN AMBIENT URBAN ATMOSPHERE

Date	Period	Total PCB Concentration (ng/m^3)*
11/20/75	1200-1600	9
11/20/75	1200-1800	8
11/20/75	1800-2400	9
11/20/75	2000-2400	7
11/21/75	2400-0600	4
11/21/75	0600-1200	6

*Reported as decachlorobiphenyl.

Environmental Protection Agency (EPA) Region II personnel employed the high-volume sampling method using polyurethane foam to assess ambient airborne concentrations of PCB in the vicinity of a major industrial user. The samples collected by EPA personnel were analyzed in this laboratory. This sampling effort provided preliminary field test conditions for relatively high airborne concentrations.

Two polyurethane foam plugs were used in the standard high-volume sampler. Each sampler was operated for a period of 4 hours. Both plugs were analyzed together, so collection efficiency cannot be determined.

Figure 18(b) shows the chromatogram of the polyurethane plug extracts. A standard Aroclor 1016 pattern is shown in Figure 18(a). Those peaks designated by a "●" match corresponding peaks in the Aroclor 1016 standard. Those designated by an "x" do not match Aroclor peaks. The elution pattern closely resembles that of Aroclor 1016. Four peaks in the pattern do not correspond with Aroclor peaks. Two of these resemble PCN, but this has not been confirmed. Quantitation of the three samples taken in the area yielded airborne concentrations of 498 ng/m^3, 400 ng/m^3, and 300 ng/m^3 as Aroclor 1016.

Confirmation of the PCB present was obtained by gas chromatography/mass spectrometry (GC/MS). An AEI Model 30 (Associated Electrical Industries) GC/MS was used with the OV-17/QF-1 column under the operating conditions described in the appendix, except helium was used in place of nitrogen for the carrier gas. The results of GC/MS analysis are depicted in Figure 19. The GC/MS was operated in the peak monitoring mode at mass values corresponding to each of the major PCB species. Good correspondence may be seen between the patterns for Aroclor 1016 and the airborne sample for trichlorobiphenyl and tetrachlorobiphenyl. Semi-quantitative information can be gained by comparing peak heights of the sample and the standard in this mode of operation. When this is done, it is apparent that trichlorobiphenyl is enriched in the sample relative to Aroclor 1016 and tetrachlorobiphenyl is reduced in the sample relative to Aroclor 1016. That is, the ratio of trichlorobiphenyl concentration to tetrachlorobiphenyl concentration in the air sample is significantly greater than the Aroclor 1016 standard. This indicates the effect of selective transport of the trichlorobiphenyl species which are generally more volatile than the tetrachlorobiphenyl species. GC/MS and GC/EC analysis also indicated the absence of monochlorobiphenyl species and the presence of trace amounts of the dichlorobiphenyl species.

High-volume air samples were collected near an electric power substation and transformer storage facility operated by a small electric cooperative in northern Florida. The sampler was placed approximately 20 meters

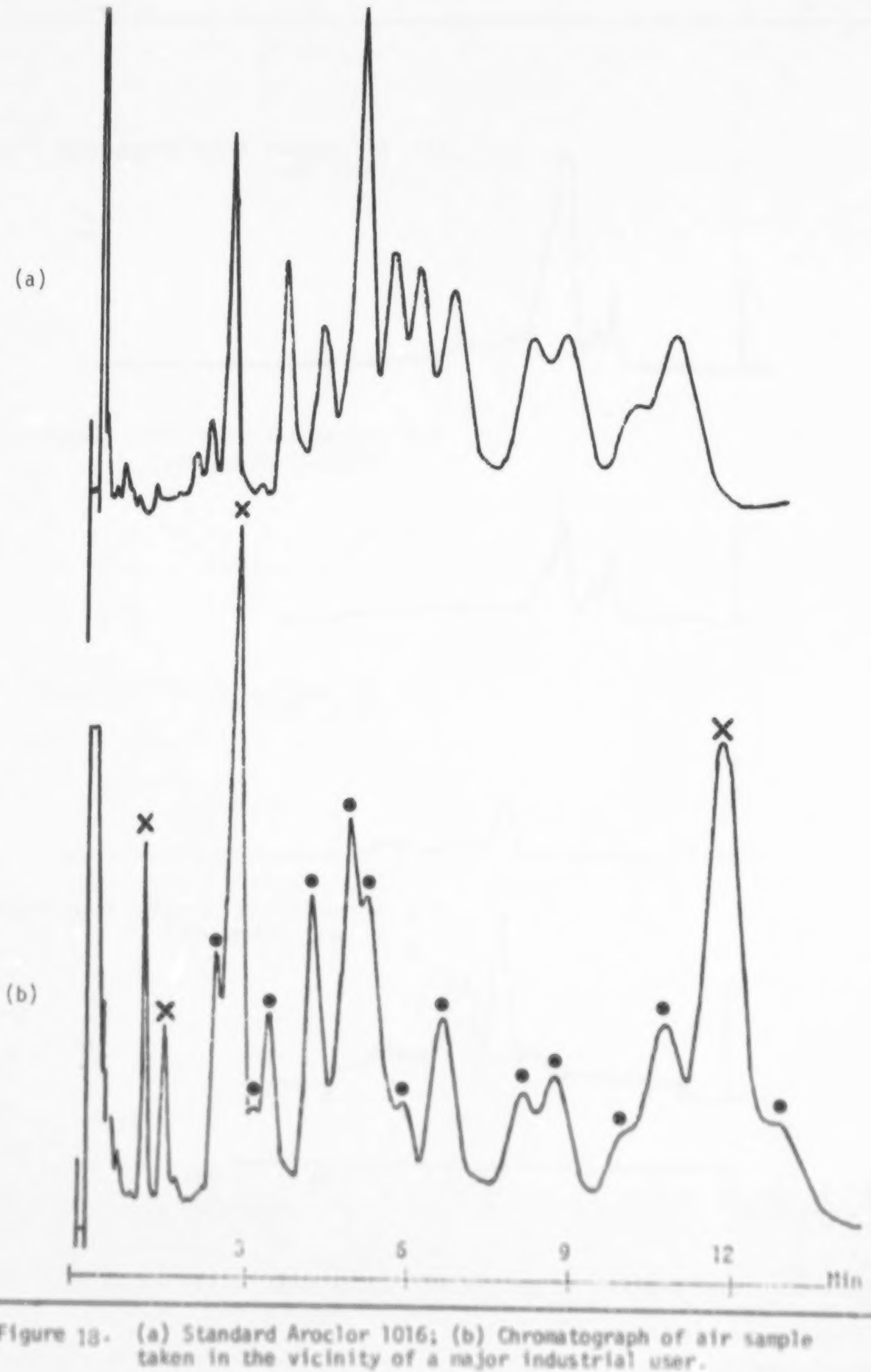

Figure 18. (a) Standard Aroclor 1016; (b) Chromatograph of air sample taken in the vicinity of a major industrial user.

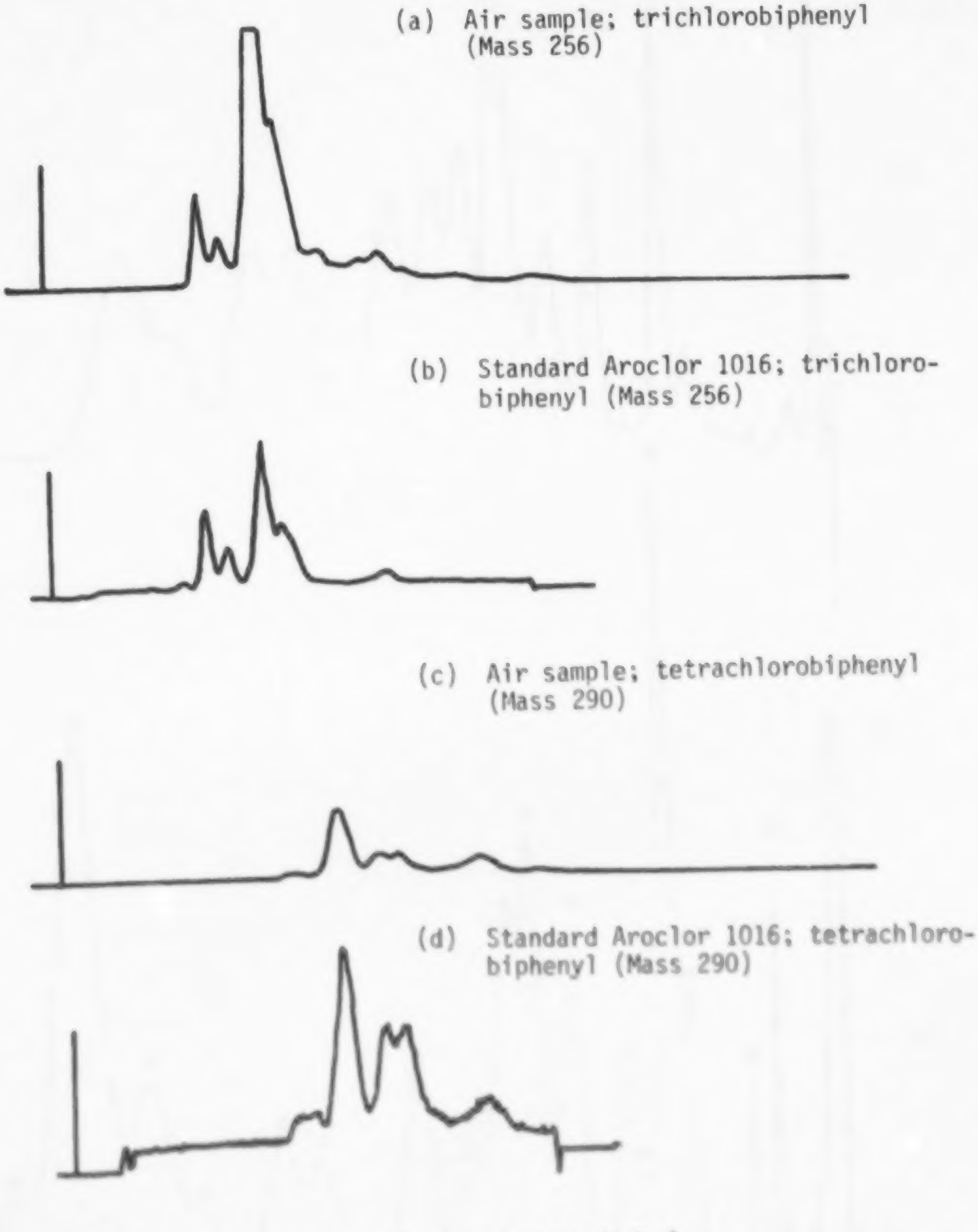

Figure 19. GC/MS analysis of ambient air sample taken in the vicinity of a major industrial user of PCB. All chromatograms are taken in peak monitoring mode at the mass indicated.

from the transformer storage area and 100 meters from the substation. Analysis was by gas chromatography using an electron capture detector (GC/EC) and confirmation was obtained by GC/MS. The analytical results are summarized in Table 17. Biphenyl was found to be present at an estimated concentration of 15 ng/m^3. This was detected by GC/MS. Nonquantifiable traces of monochlorobiphenyl and dichlorobiphenyl were detected by GC/EC and confirmed by GC/MS. Most PCB present appeared by both GC/EC and GC/MS analysis to be trichlorobiphenyl. A concentration of 30 ng/m^3 was estimated for this species. Tetrachlorobiphenyl was also present at 6 ng/m^3.

TABLE 17

RESULTS OF HIGH-VOLUME AMBIENT AIR SAMPLE TAKEN IN THE VICINITY OF AN ELECTRICAL SUBSTATION AND TRANSFORMER STORAGE FACILITY

Species	Analytical Method		Concentration (ng/m^3)
	GC/EC	GC/MS	
biphenyl	ND	X	15 ng/m^3 (est.)
monochlorobiphenyl	X, trace	X, trace	1 ng/m^3 (est.)
dichlorobiphenyl	X, trace	X, trace	no est.
trichlorobiphenyl	X, strong	X, strong	30 ng/m^3
tetrachlorobiphenyl	X	X	6 ng/m^3

Sampled 180 minutes total of 185 m^3 of air drawn. No PCB was present in substitution greater than tetrachlorobiphenyl.

X = detected
ND = not detected

These preliminary field tests provided some experimental data that applies to practical application of the method under field conditions. The preliminary exprimental field data were of value in development of the method suitablefor routine field use. These preliminary field data do not, however, costitute a field test of the method since significant changes were incorporated into the method as a result of this field experience. The following section describes valid field tests of the final method for PCB in air as described in Appendix A.

3.3 FIELD TESTS OF THE FINAL METHOD

The sampling and analytical method, as described in Appendix A, was field tested on several occasions in Gainesville, Florida, and on two occasions in New Bedford, Massachusetts. The procedure was followed as written without deviation. In each sample, the glass fiber filter and each of the three polyurethane foam (PUF) plugs were analyzed separately. Airborne PCB concentrations were measured over the range of 4 ng/m^3 to 1.4 ug/m^3 during these field tests under a variety of ambient temperature and humidity conditions.

3.3.1 Tests in Gainesville, Florida

Table 18 is a summary of the results of several field tests conducted over a 9-month period in Gainesville, Florida. Sampling periods range from 30 minutes to 12 hours. Measured airborne PCB concentrations varied from 11 ng/m^3 to 44 ng/m^3 as DCB. On the average, 94 $\pm$ 3 percent of the PCB captured from the atmosphere was retained on the filter and first two PUF plugs. There are no apparent effects of ambient temperature or humidity on collection efficiency over the ranges encountered during these field tests. There is also no statistically significant correlation between collection efficiency and sample flow rate or duration.

Figures 20 through 23 illustrate the GC/EC chromatograms for the test conducted on July 26, 1977. Figure 20(a) shows the chromatogram of an unexposed PUF plug from the set of plugs used in the tests. No detectable PCB is present. Figure 20(b) is a chromatogram of the glass fiber filter extract from the 2-hour ambient sample taken on that date. Perchlorination yielded a concentration of 74 ng PCB as DCB on this filter, which is below the detection limit by pattern quantitation. Figure 21 is a chromatogram of an Aroclor 1242 standard. Figure 22 is

TABLE 18

RESULTS OF FIELD TESTS CONDUCTED IN GAINESVILLE, FLORIDA

Sample Date	4/22/77	4/22/77	4/27/77	7/26/77 †	10/31/77*	11/20/77**
Sample Time	1155-1225	1535-1635	1043-1231	1255-1458	1108-1308	1216-1815
Sample Duration (min)	30	60	108	123	120	359
Flow Rate (m^3/min)	0.95	1.0	0.97	0.91	0.72	1.0
Vol. Air Sampled (m^3)	29	60	105	112	86	360
Ambient Temp. (°C)	32	32	22	35	23	26
Ambient Humidity (%)	39	39	38	39	73	56
PCB Collected (ng @ DCB)						
Filter	55	466	82	74	73	35
PUF #1	681	1180	2330	2720	660	5890
PUF #2	321	830	422	763	110	210
PUF #3	163	142	286	350	84	54
Total	1220	2618	3120	3907	927	6189
Percent of Total Collected						
Filter	45	18	26	1.9	7.9	0.6
PUF #1	61	45	75	70	71	95
PUF #2	29	32	14	20	12	3.4
PUF #3	13	5	9	8.1	9.1	1.0
Filter + PUF #1 + PUF #2	94.5	95.0	91.6	92.0	90.9	99.0
Airborne Conc. (ng/m^3 @ DCB)	43	44	30	35	11	17

† Chromatogram shown in Figures 20, 22, and 23.

* Chromatograms shown in Figure 24.

** Quantitated by pattern matching and mathematically converted to DCB, chromatograms shown in Figures 25 and 26 (a)(b)(c).

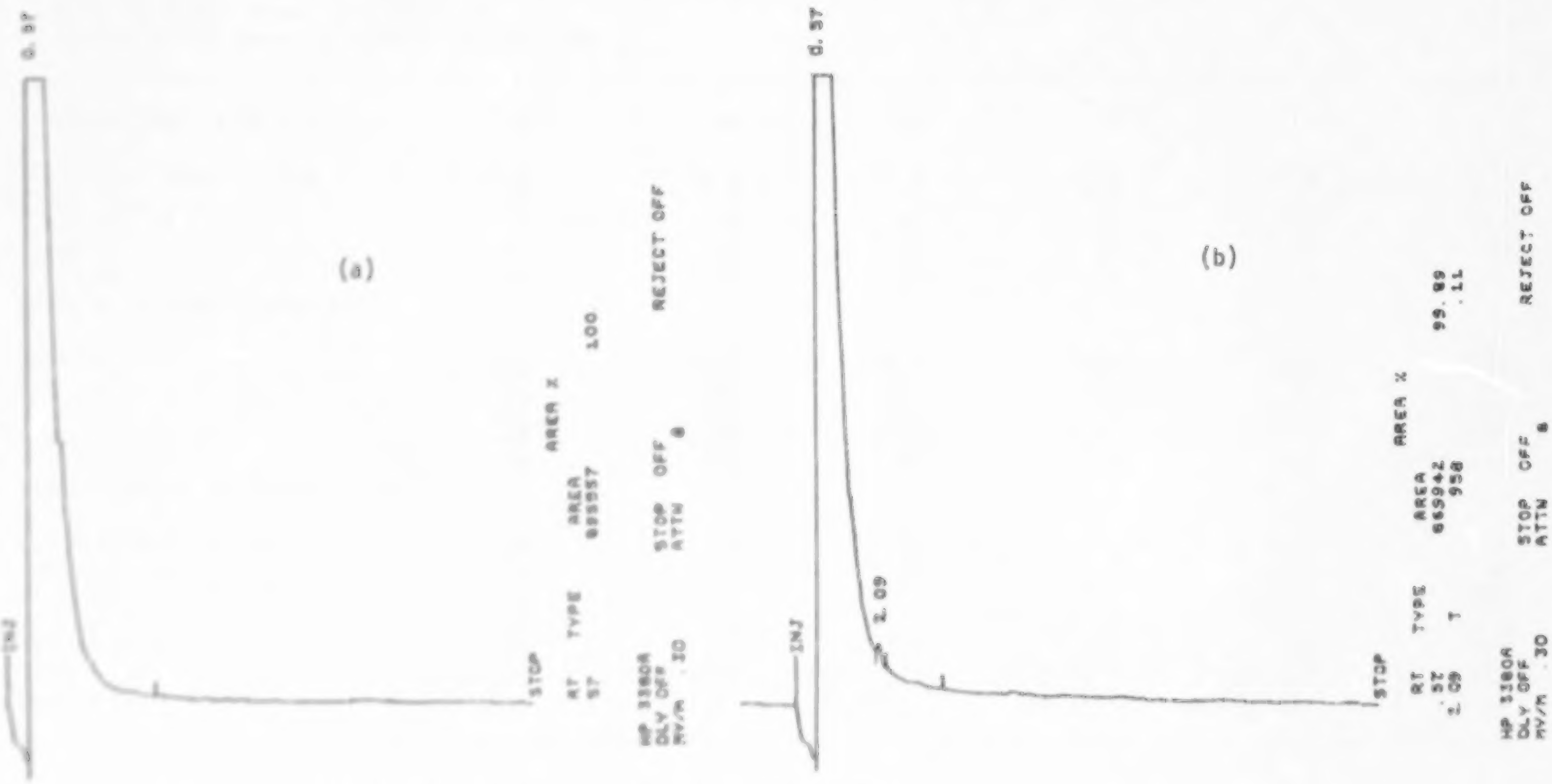

Figure 20. (a) GC/EC Chromatogram of an Unexposed PUF Plug.
(b) GC/EC Chromatogram of the Glass Fiber Filter Used During the Field Test on 7/26/77.

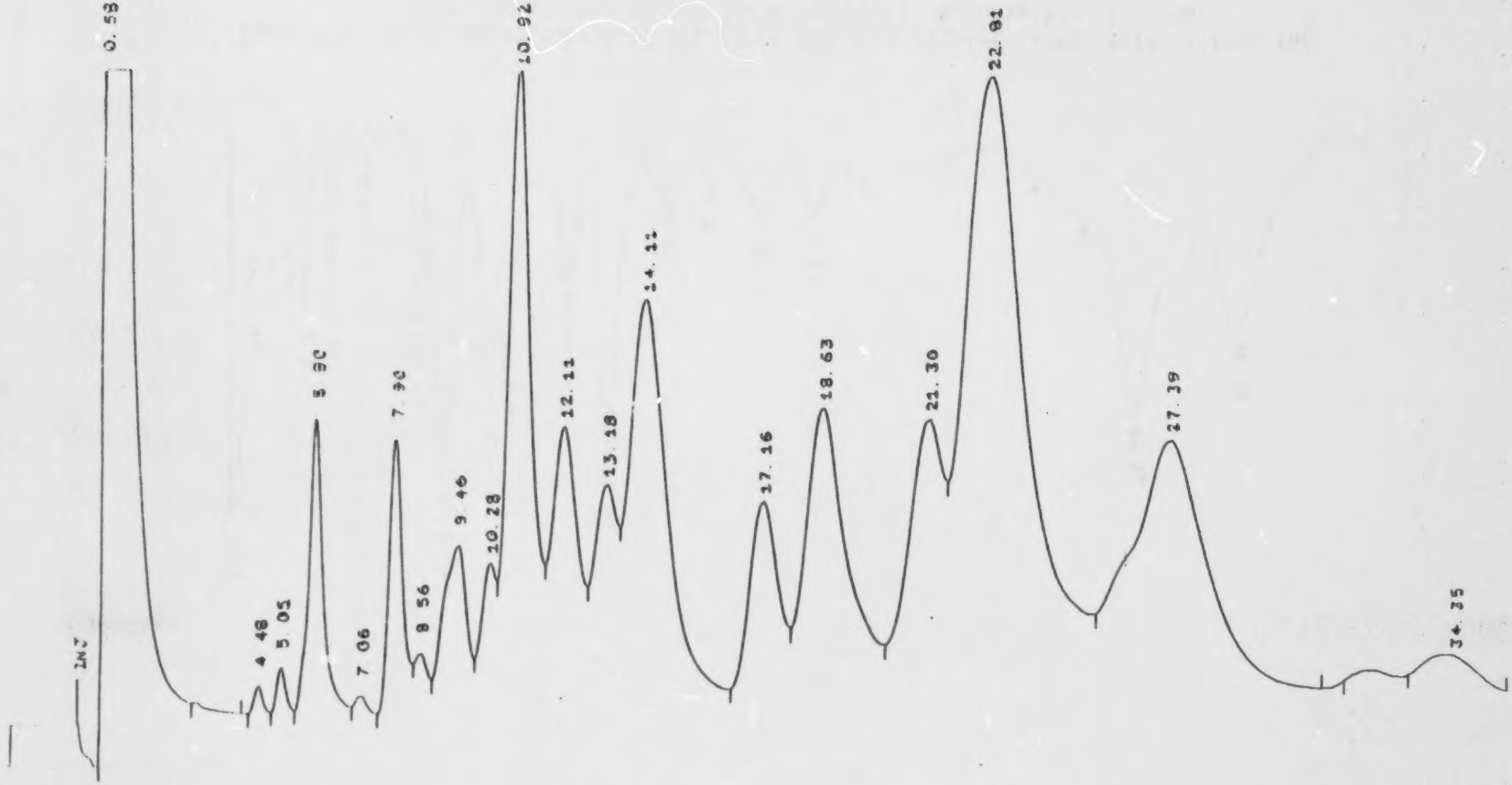

Figure 21. GC/EC Chromatogram of an Aroclor 1242 Standard.

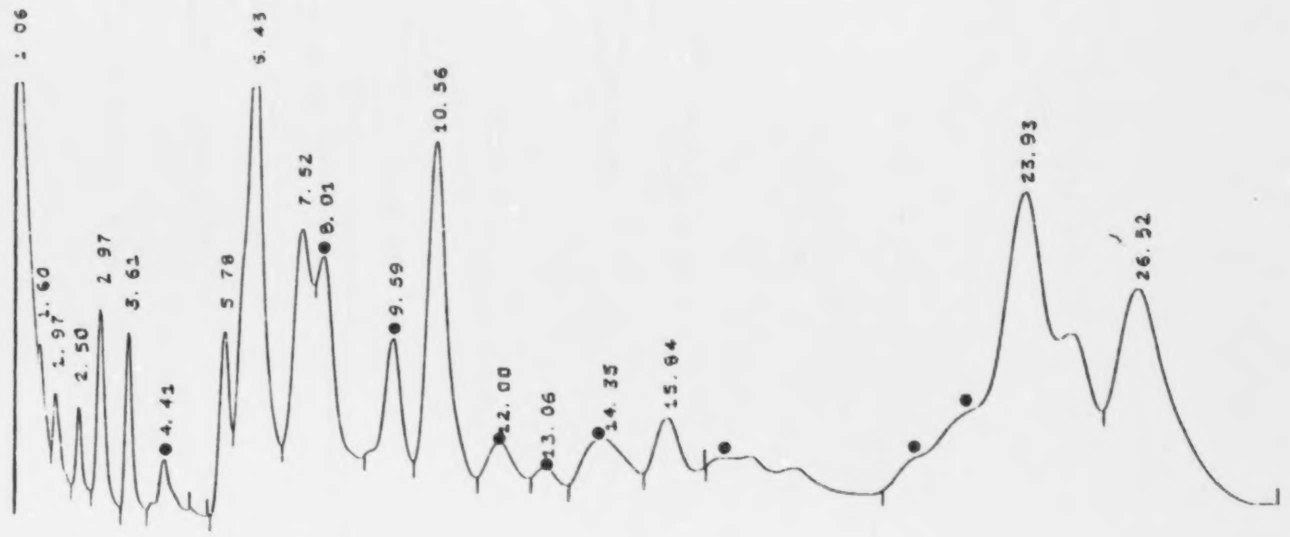

Figure 22. GC/EC Chromatogram of the First PUF Plug Extract (Attn: 8×10^{-9}) from the 2-Hour Ambient Air Sample Taken 7/26/77 in Gainesville, Florida.

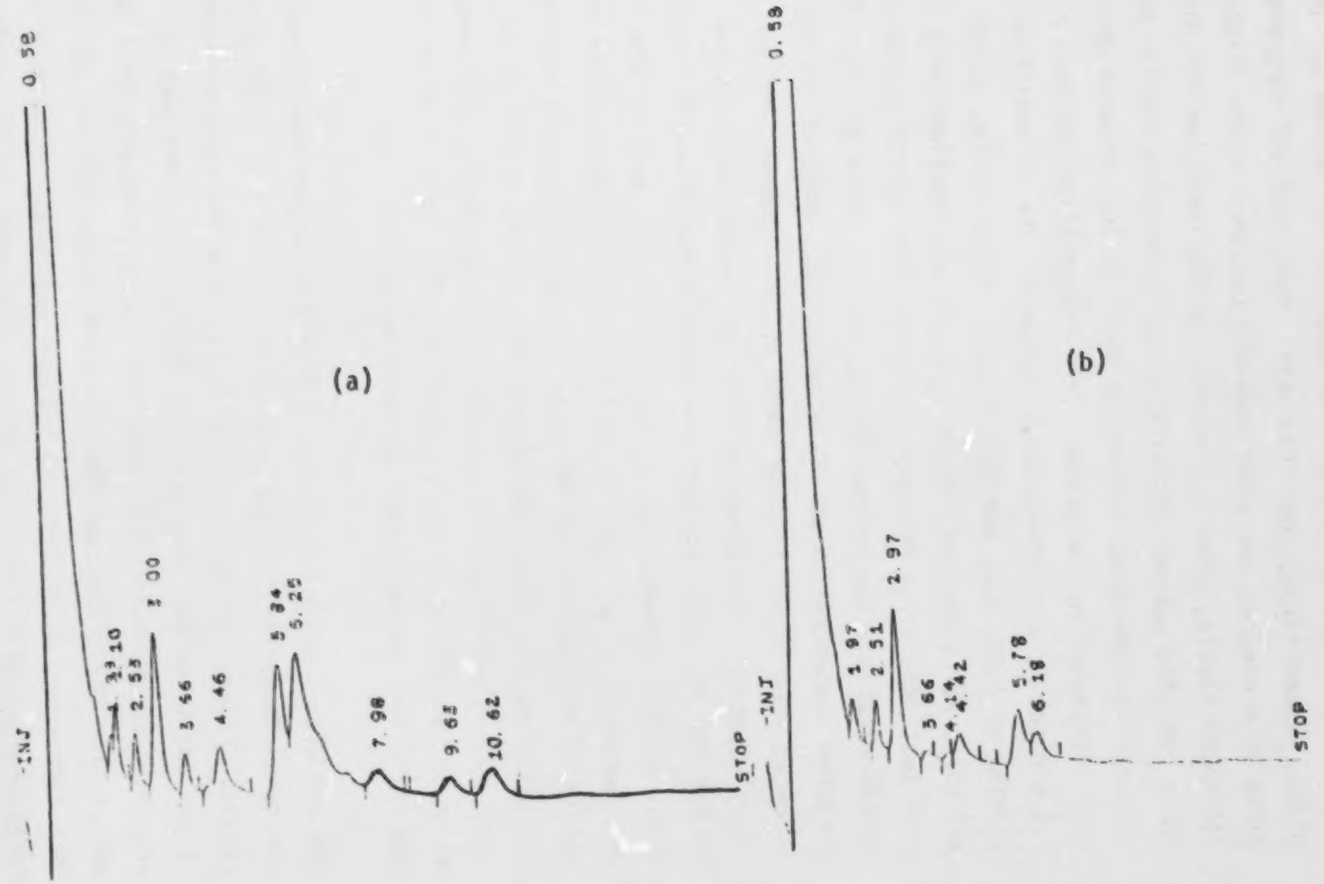

Figure 23. GC/EC Chromatogram of (a) the Second and (b) the Third PUF Plug Extracts (Attn: 8×10^{-9}) from the 2-Hour Ambient Air Sample Taken 7/26/77 in Gainesville, Florida.

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the chromatogram of the extract of the first PUF plug in the sampler. Those peaks denoted by a "●" coincide with peaks in Aroclor 1242. Figures 23(a) and (b) are chromatograms of the second and third PUV plugs, respectively, from this test. Note that all compounds eluting after 10.6 minutes are quantitatively captured on the first PUF plug and all those eluting after 6.2 minutes on the first two PUF plugs. The third PUF plug extract contains no peaks matching Aroclor peaks. The unidentified compounds eluting at 15.8 and 10.6 minutes are captured with high efficiency in the system. The unidentified compound eluting at 3.6 minutes is also effectively captured. The unidentified compounds eluting at 1.97, 2.5, and 3.0 minutes, respectively, appear to saturate all three PUF plugs and, hence, are probably ineffectively captured. In this test, the first PUF plug contained 2720 ng PCB as DCB upon perchlorination, the second 763 ng, and the third 350 ng. The measured airborne concentration was 35 ng/m^3 as DCB. Most of the PCB peaks detected were in the elution range of tri-, tetra-, and pentachlorobiphenyl species. The 2-hour ambient air sample taken in the same location on October 31, 1977, yielded the chromatogram shown in Figure 24(a). Peaks in this chromatogram which coincide with Aroclor peaks are designated by a "●", but the pattern match is poor. After perchlorination of the extract, as shown in Figure 24(b), quantitation is direct and unequivocal. This sample contained 660 ng as DCB on the first PUF plug, 110 ng on the second, and 84 ng on the third. The measured airborne concentration was 11 ng/m^3 as DCB. This is approximately one-third the ambient level measured on July 26, 1977.

PCB collection efficiency remains high for longer than 2-hour sampling periods. Therefore, it may be desired to obtain a longer time-integrated sample. Figures 25 and 26(a), (b), (c) show the chromatograms of the filter and three PUF plug extracts from a 6-hour air sample. PCB species are found on the first and second PUF plugs (indicated by a "●"), but are absent from the filter and the third PUF plug. MCB was not detected. This sample was quantitated by pattern matching, yielding an airborne concentration of 8.8 ng/m^3 as Aroclor 1242 or 17 ng/m^3 as DCB. The pattern most closely resembles Aroclor 1242, but not all peaks are present. Hence, the concentration reported incorporates the uncertainty inherent in the pattern quantitation method.

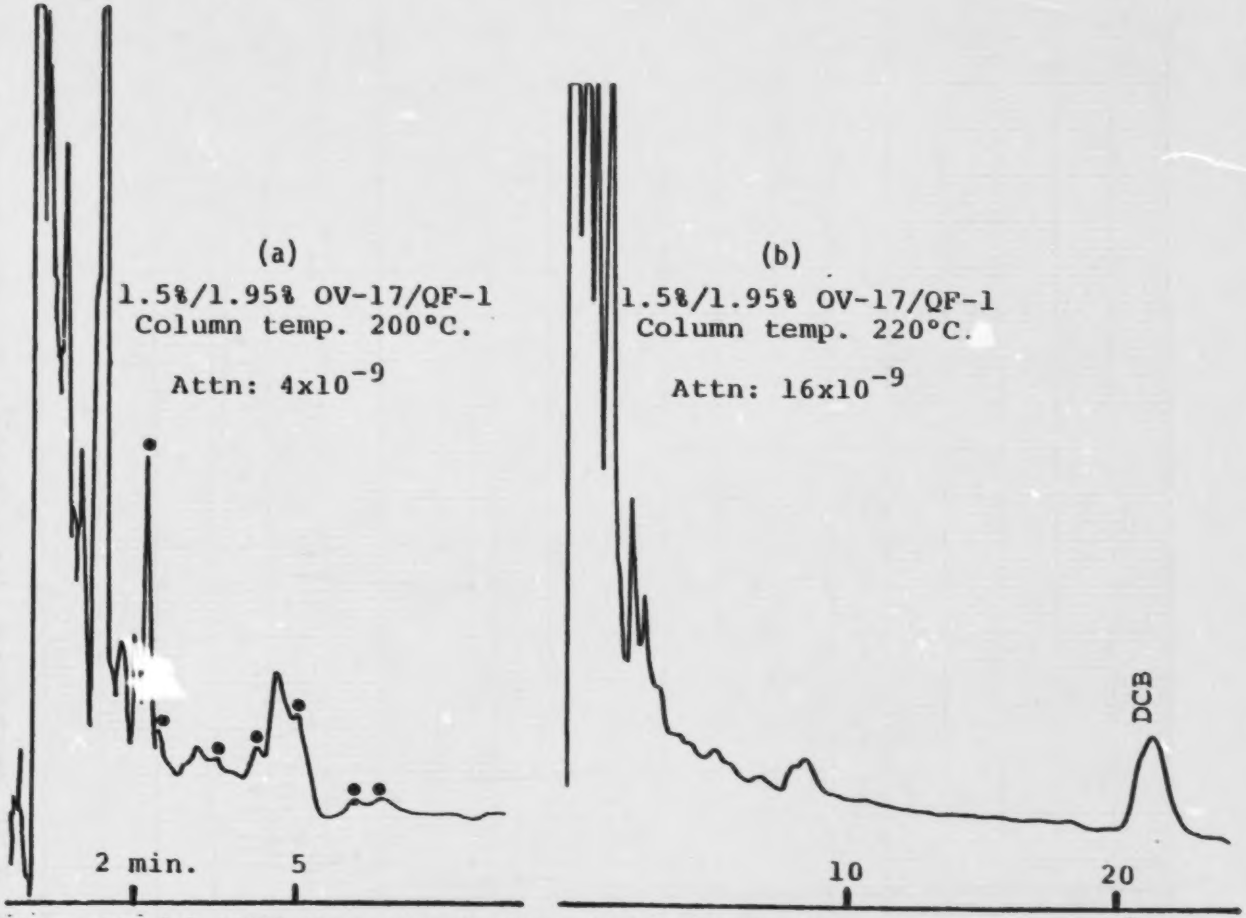

Figure 24. (a) GC/EC Chromatogram of the First PUF Plug Extract (Attn: 4 x 10^{-9}) from the 2-Hour Ambient Air Sample Taken 10/31/77 in Gainesville, Florida.
(b) GC/EC Chromatogram of the Same Sample (Attn: 16 x 10^{-9}) After Perchlorination.

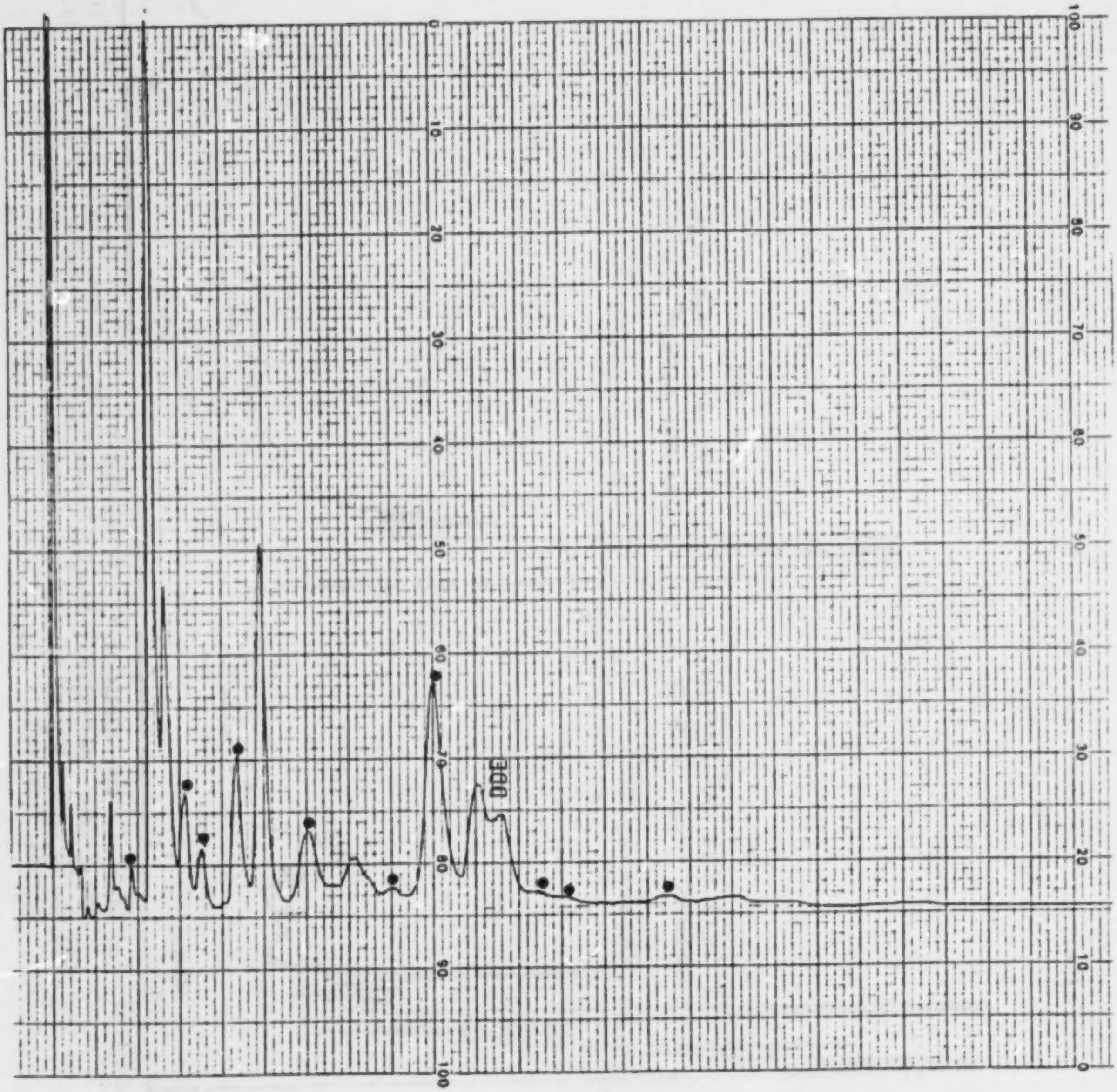

Figure 25. GC/EC Chromatogram (Attn: 16×10^{-9}) of 6-Hour Ambient Air Sample (PUF #1) Taken 11/20/77 in Gainesville, Florida.

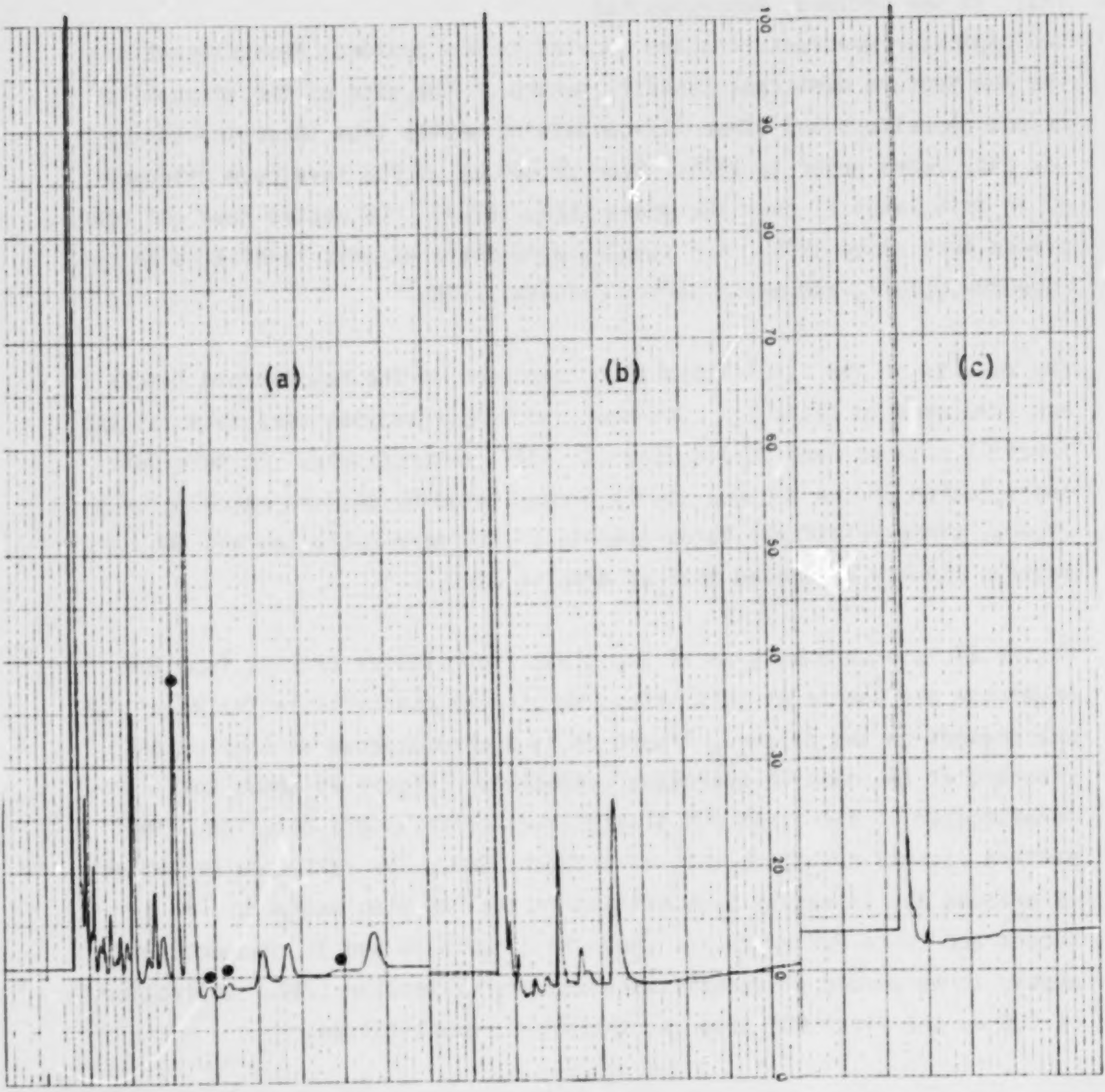

Figure 26. GC/EC Chromatograms of (a) Second PUF Plug, (b) Third PUF Plug, and (c) Glass Fiber Filter (Attn: 16×10^{-9}) of 6-Hour Ambient Air Sample Taken 11/20/77 in Gainesville, Florida.

It may be noted in Figure 25 that DDE is apparently present in this air sample and is quantitatively captured (cf. Figure 26) on the first PUF plug, although this peak has not been confirmed by mass spectrometry. The sampling system would, therefore, serve as well for the measurement of airborne DDE concentration.

3.3.2 Tests in New Bedford, Massachusetts

Two capacitor manufacturers are located in New Bedford, Massachussetts. The New Bedford municipal landfill served as the site of the disposal of reject capacitors and other PCB-containing wastes from these industries for many years prior to 1975. Over 22,000 kg of PCB have been disposed of in this landfill over the years (EPA, 1976). PCB wastes have not been placed here since 1975. Air samples were taken at this landfill site on June 28-30,1977, and again during January, 1978.

The results of the first field test conducted at the New Bedford landfill are tabulated in Table 19. One-hour and 6-hour samples were taken at the landfill site on June 28 and June 30, 1977, respectively. In this case, quantitation of the PCB was easily accomplished by pattern matching techniques, since relatively large amounts of PCB were collected and the pattern closely resembled that of Aroclor 1242.

Figure 27 is a chromatogram of the glass fiber filter extract from the 60-minute air sample at this site. Marginally quantifiable traces of PCB are present on the filter. Figure 28 is a chromatogram an Aroclor 1242 standard at the same GC operating conditions. Figure 29 shows the chromatogram of the first PUF plug extract after an 8:1 dilution. The pattern closely resembles that of Aroclor 1242. The full Aroclor pattern is present and is easily quantifiable in the PUF plug extract. The second and third PUF extracts, shown in Figures 30 and 31, respectively, appear to be devoid of quantifiable amounts of Aroclor 1242. Collection of PCB on the first PUF plug is, therefore, quantitative.

On Figure 29, the "x" denotes the retention times of o,p'-DDT and p,p'-DDT. It appears, but has not been confirmed by mass spectrometry,

TABLE 19

RESULTS OF FIELD TESTS CONDUCTED IN NEW BEDFORD, MASSACHUSETTS, IN JUNE, 1977

Sample Date*	6/28/77 †	6/28/77	6/30/77
Sample Time	1059-1159	1059-1159	0930-1540
Sample Duration (min)	60	60	370
Wind Direction	WSW	WSW	NW
Wind Speed (mph)	10	10	12-15
Sample Flow Rate (m^3/min)	1.02	1.02	1.15
Vol. Air Sampled (m^3)	61	61	426
PCB Collected (ug Aroclor 1242)			
Filter	0.2	0.2	14.9
PUF #1	53.9	82.1	134
PUF #2	<0.2	<0.2	17.9
PUF #3	<0.2	<0.2	4.8
Total	54.1	82.3	172
Percent of Total PCB Collected			
Filter	0.4	<0.4	8.7
PUF #1	99.6	99.8	78.0
PUF #2	<0.4	<0.4	10.5
PUF #3	<0.4	<0.4	2.8
Filter + PUF #1 + PUF #2	100.0	99.8	97.2
Airborne PCB Conc. (ug/m^3 Aroclor 1242)	0.89	1.3	0.40
Biphenyl Collected (ng/m^3)	<0.5	--	<0.5

* Ambient temperature 25°C.

† Chromatograms shown in Figures 27, 29, 30, and 31.

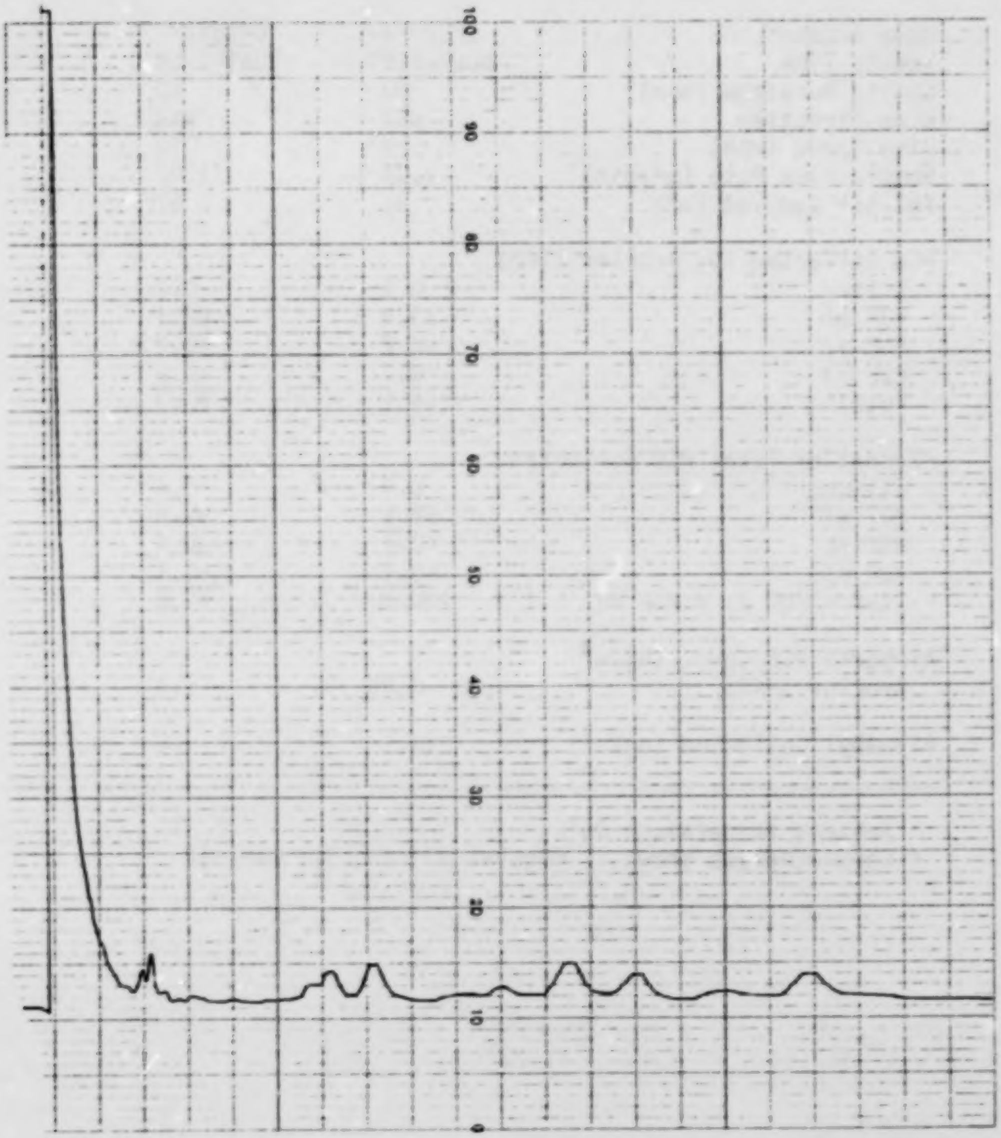

Figure 27. GC/EC Chromatogram of the Filter Extract (Attn: 16×10^{-9}) from the 60-Minute Ambient Air Sample Taken at New Bedford Landfill.

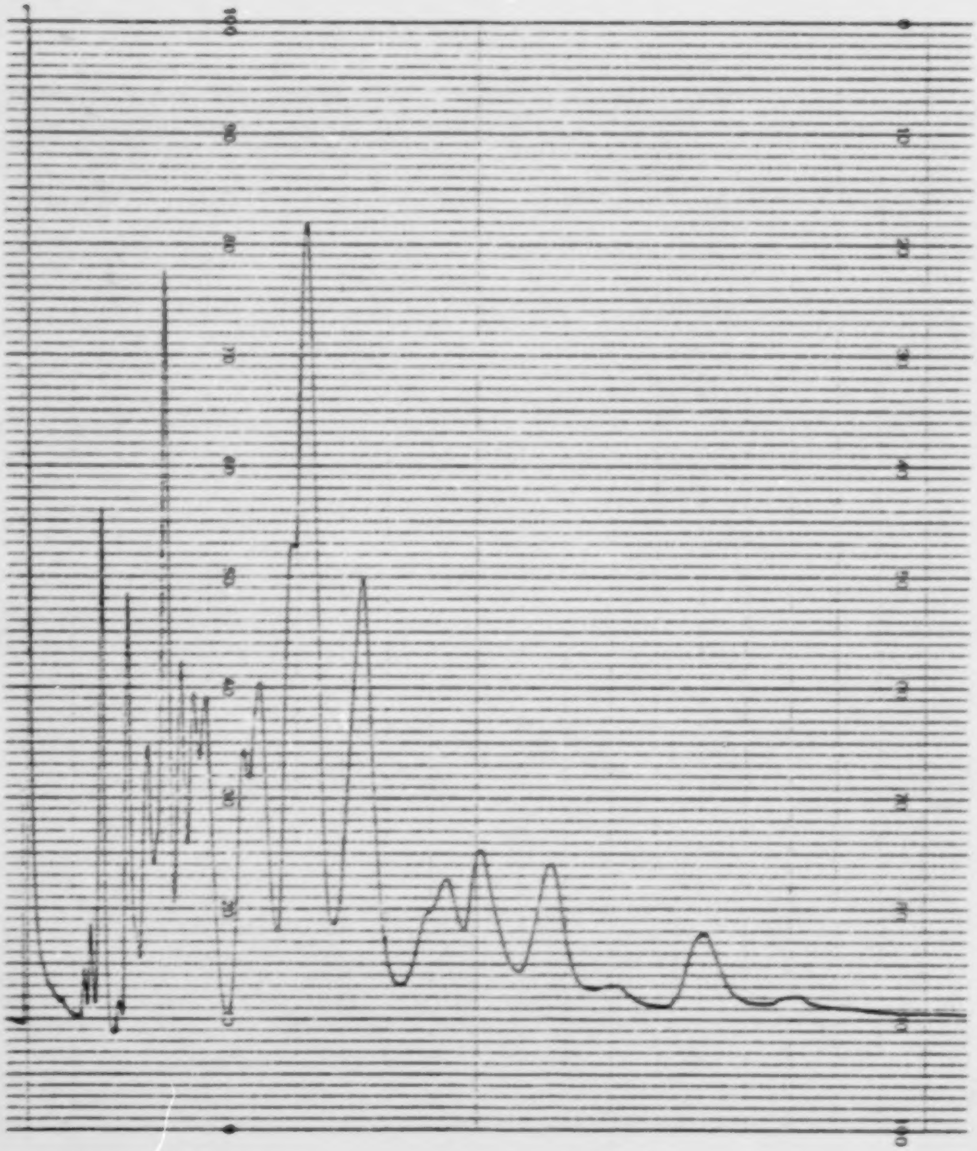

Figure 28. GC/EC Chromatogram (Attn: 16×10^{-9}) of an Aroclor 1242 Standard.

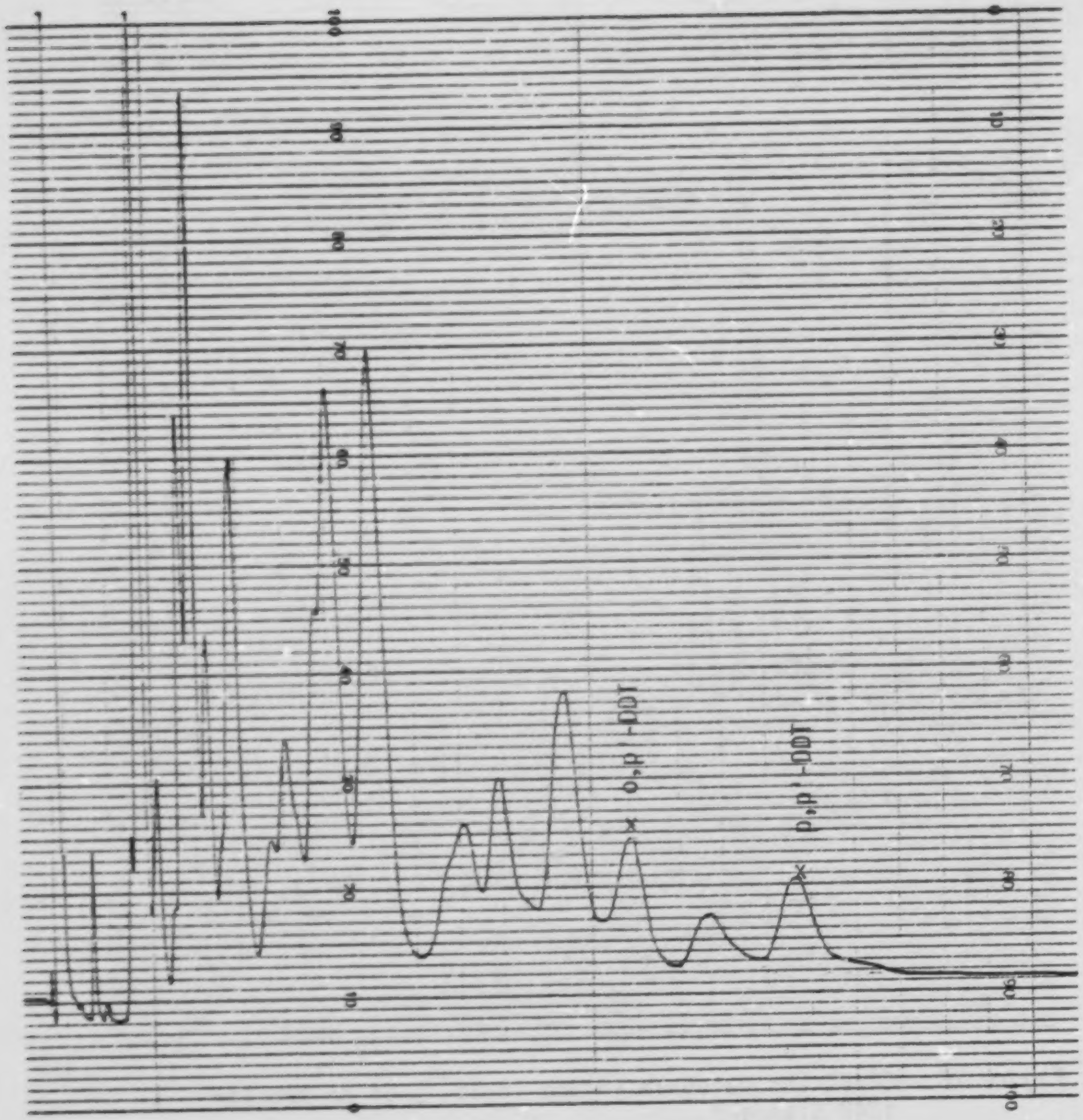

Figure 29. GC/EC Chromatogram of the First PUF Plug Extract (Attn: 16x10^{-9} Diluted to 1/8) of the 60-Minute Ambient Air Sample Taken at New Bedford Landfill.

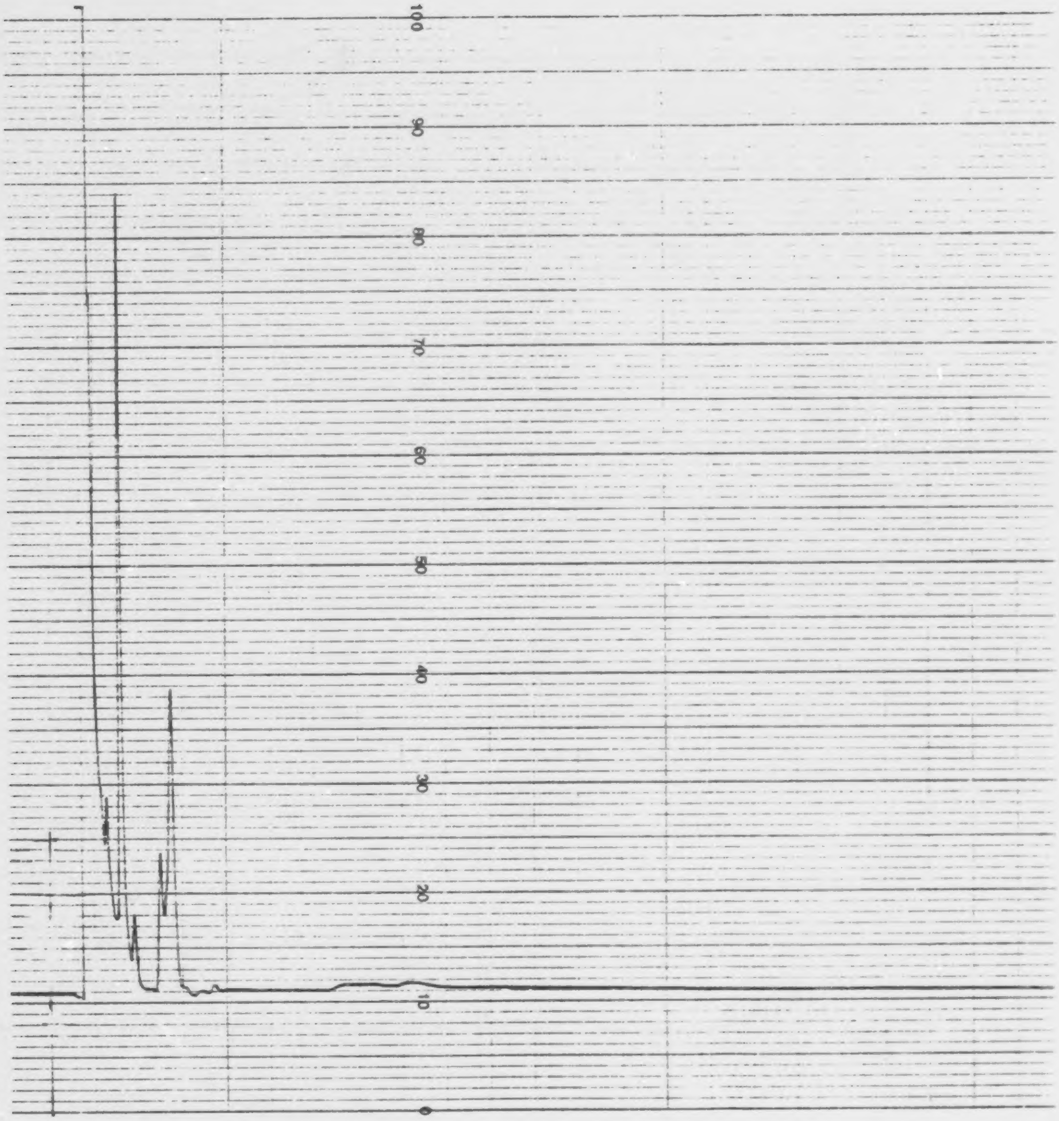

Figure 30. GC/EC Chromatogram of the Second PUF Plug Extract (Attn: 16x10^{-}
of the 60-Minute Ambient Air Sample Taken at New Bedford Landfi

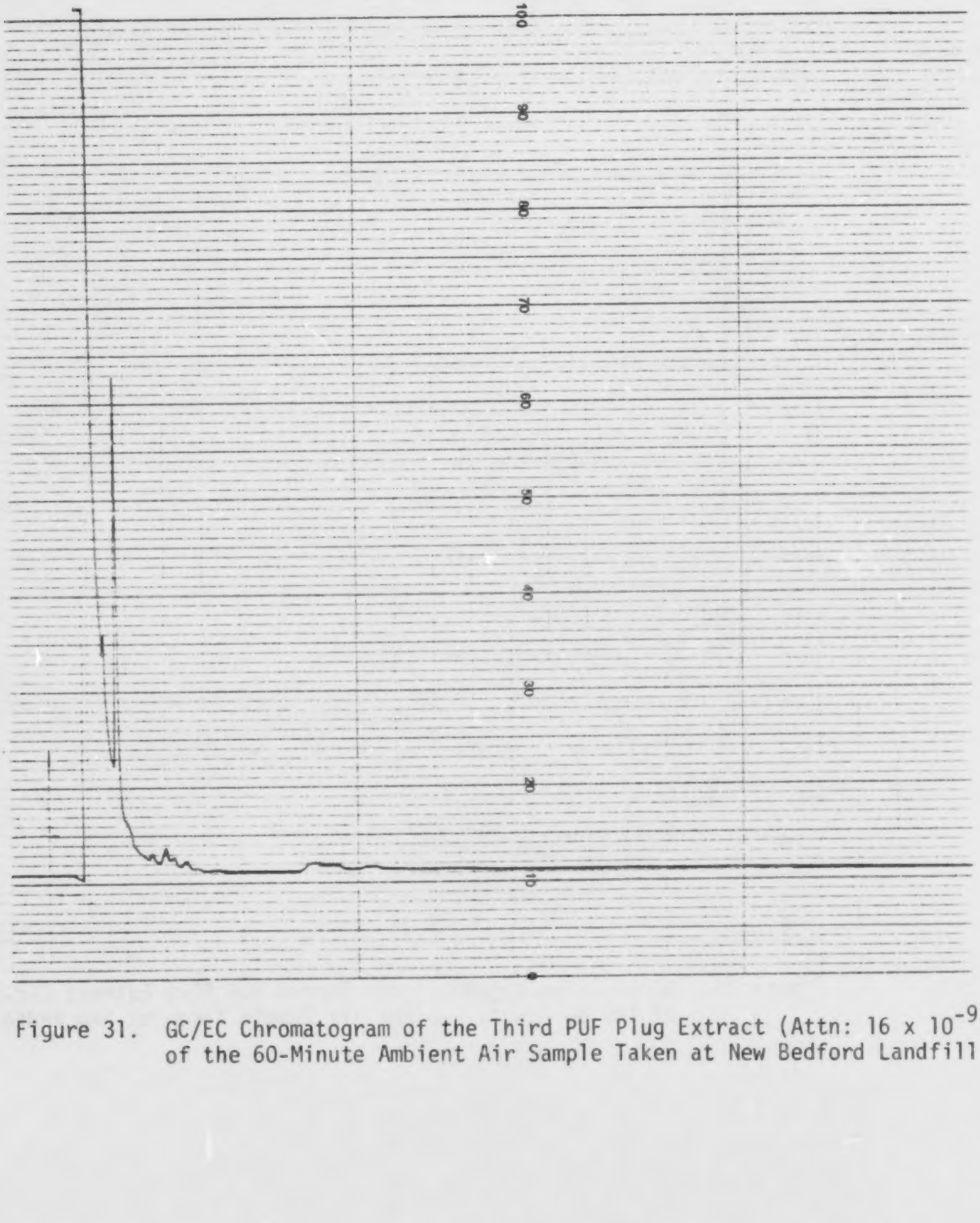

Figure 31. GC/EC Chromatogram of the Third PUF Plug Extract (Attn: 16 x 10^{-9}) of the 60-Minute Ambient Air Sample Taken at New Bedford Landfill.

that DDT is also present in these air samples and is quantitatively captured on the first PUF plug.

The extracts from the 60-minute air samples were then perchlorinated for confirmation of the PCB. The results were as follows:

filter	173	ng DCB
PUF #1	72,800	ng DCB
PUF #2	129	ng DCB
PUF #3	43	ng DCB

PCB is confirmed and the high collection efficiency is validated by perchlorination. The total amount of DCB in the filter and first PUF plug extracts (73 ug) can be converted to equivalent Aroclor 1242 using the conversion factor in Table 1 of Appendix A. Applying this conversion, an equivalent of 0.62 ug/m^3 of Aroclor 1242 is calculated. This compares to 0.89 ug/m^3 determined by pattern matching. The 30 percent discrepancy in the amount measured by the two methods in this case may be attributed to two factors: (a) the large amount of dilution required to quantitate the first plug extract in effect results in a multiplication of analytical variability; and (b) it is assumed, both for pattern quantitation and for conversion of perchlorination results to equivalent Aroclor 1242, that Aroclor 1242 is present alone and in unmodified form. These necessary assumptions limit the degree of agreement that may be expected between pattern quantitation and perchlorination results. It would not normally be necessary to perchlorinate such high level samples, however, for purposes of quantitation.

The samples taken in the vicinity of the New Bedford landfill were also checked for the presence of biphenyl (BIPH) using the analytical method described in Appendix A (Section 12.0). BIPH was absent from all 1-hour and 6-hour filter and PUF plug extracts. Hence, BIPH was collected in concentrations below the detection limit of 0.5 ng/m^3, if at all. Figure 32 is a GC/FID (flame ionization detector) chromatogram of a BIPH standard. Figure 33 is a chromatogram of the first PUF plug extract from the 60-minute sample. Note the absence of a BIPH peak in Figure 33.

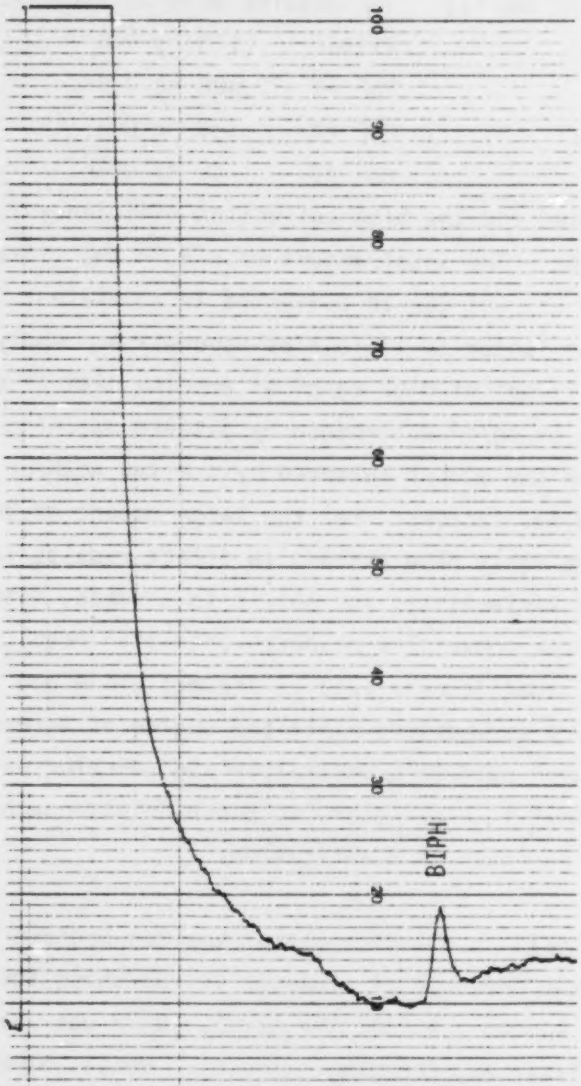

Figure 32. GC/FID Chromatogram of Biphenyl at 2.8 ng.

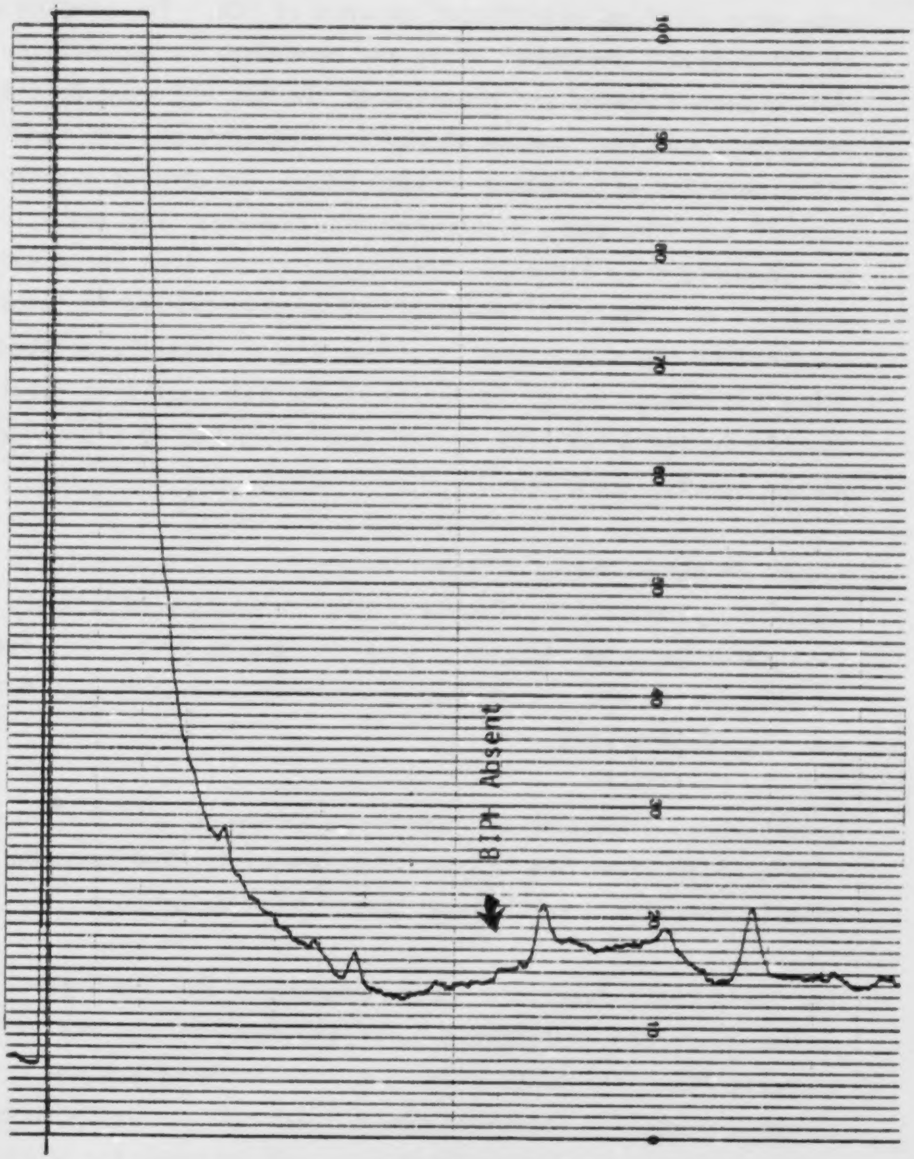

Figure 33. GC/FID Chromatogram of the First PUF Plug Extract from the 60-Minute Ambient Air Sample Taken at New Bedford Landfill

Since relatively high airborne PCB levels were detected over the New Bedford landfill, a second sampling trip was scheduled in January, 1978, in an attempt to determine if the landfill itself was the source of the airborne PCB, or if one or more of the other potential sources in the area were emitting significant amounts of PCB. The samping was conducted by EPA Region I personnel using the procedure in Appendix A. Sampling was conducted upwind and downwind of the two PCB user facilities in the area, the municipal sewage sludge incinerator, and the landfill. Sampling duration was 3 hours in each case. The ground was frozen at the time of sampling and a light snow was falling. The analytical results are summarized in Table 20. One may conclude from these data that the landfill is a possible low-level PCB emitter during the winter months as compared to the summer months. Some PCB is possibly emitted from the municipal sewage sludge incinerator, but PCB user A is clearly a major emitter in the area. PCB user B apparently had no significant emissions at the time of sampling.

Figure 34 shows the GC elution pattern for the sample taken over the landfill. The pattern closely resembles Aroclor 1016/1242. Each peak designated by a "●" matches a peak in Aroclor 1242. At lower levels such as this, it is not possible to unequivocally distinguish between these two similar Aroclors.

Figure 35(a) shows the air sample taken upwind of PCB user A, while Figure 35(b) shows the sample taken downwind. The downwind sample clearly contains a substantial amount of Aroclor 1016.

The field tests described above demonstrate the practical use of the method described in Appendix A for the sampling and analysis of ambient airborne PCB. The tests covered a wide range of ambient concentrations. In the Gainesville location, the PCB was not generally recognizable by pattern matching and perchlorination was required for quantitation, while at the New Bedford location, the PCB pattern was clear. In all field tests conducted, an average of 96 ± 4 percent of the PCB collected

TABLE 20

RESULTS OF FIELD TESTS CONDUCTED IN NEW BEDFORD, MASSACHUSETTS, IN JANUARY, 1978

Date	Site	Location	Concentration (ng/m^3)	Aroclor
1/17	landfill	upwind	8.5	1242/1016
		on site	21	1242/1016
		downwind	13	1242/1016
1/24	sewage sludge incinerator	upwind	4.3	1242/1016
		downwind	13	1242/1016
1/27	PCB user A	upwind	5.6	1242/1016
		downwind	490	1016 only
1/19	PCB user B	upwind	19	1242/1016
		downwind	5.1	1242/1016

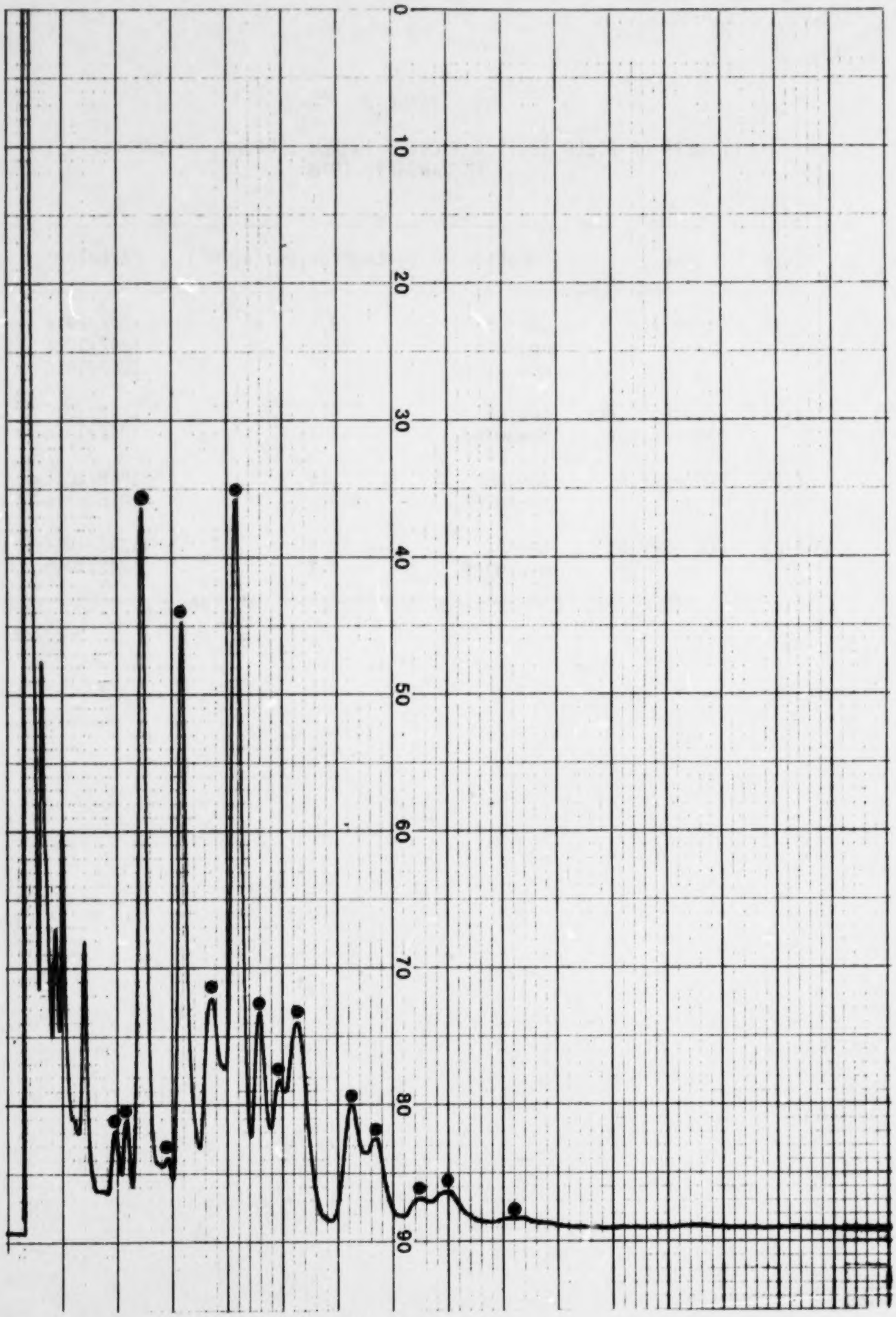

Figure 34. GC/EC Chromatogram of Air Sample Taken over New Bedford, MA, Landfill. 0.5 ul Injection, Attn: 64 x 10^{-9}

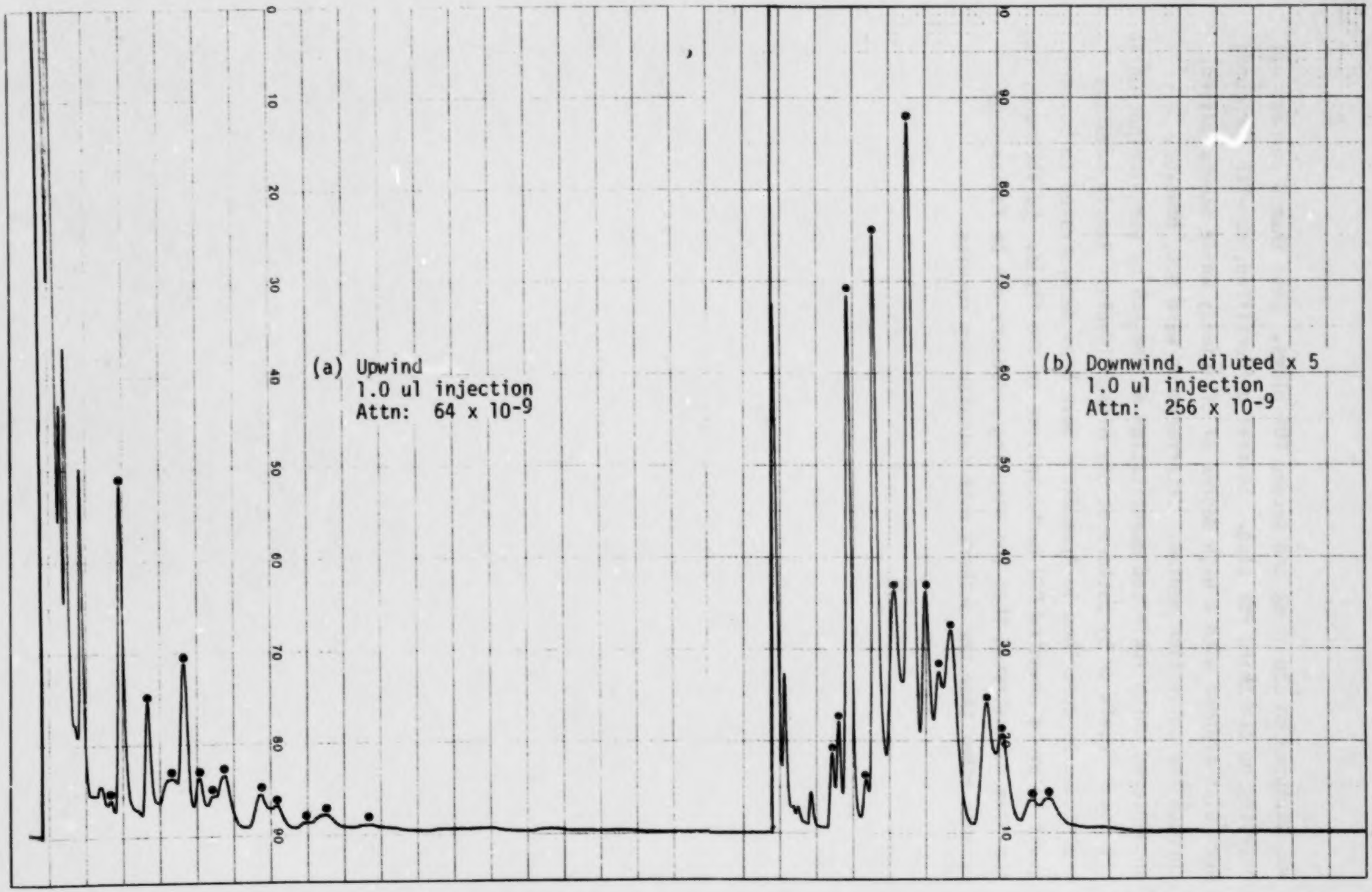

Figure 35. GC/EC chromatograms of air samples taken (a) upwind and (b) downwind of a PCB user facility.

was captured on the first and second PUF plugs. Less than 4 percent was detected on the third PUF plug. Several unidentified, non-PCB compounds were also trapped with a high degree of efficiency while others passed through the collection medium. Interferences were not, however, encountered which inhibited quantitation of the PCB by perchlorination at the lower levels or by pattern at the higher levels. Sample handling techniques as described in Appendix A have been demonstrated to be adequate to avoid unwanted PCB contamination in the field. Furthermore, it has been demonstrated that the sampling procedure can be followed by persons other than the authors with satisfactory results.

4.0 CONCLUSIONS AND RECOMMENDATIONS

A method has been developed for the sampling and analysis of polychlorinated biphenyls (PCBs) in air. An easily constructed, high-volume sampling system is employed with porous polyurethane foam as the collection medium. The sample is collected at the rate of 0.6 to 1.0 m^3/min. The method is described in detail in Appendix A.

Laboratory procedures have been developed, and are described in this document, which permit the quantitative analysis of even the most volatile PCB species in an air sample. A perchlorination technique for the quantitative analysis of PCB has been adapted for use with air samples. The technique is shown to convert even the most volatile PCB species to decachlorobiphenyl for simple and direct quantitative analysis. Data is presented to show conversion efficiencies of a variety of PCBs to decachlorobiphenyl of 101 ± 6 percent over the range of 0.103 to 10.0 ug. A ruggedness test was conducted which indicates the proposed perchlorination technique can yield reliable interlaboratory results. The perchlorination technique is a recommended optional method of quantitation of PCB when the commonly used pattern matching techniques are found to be unsuitable as a result of either low quantities of collection or poor Aroclor pattern recognition. It is the opinion of the authors that the use of the perchlorination technique is generally necessary for the analysis of low (i.e., less than 25 ng/m^3) airborne levels of PCB. The analytical method is effective for the analysis of airborne PCB levels within at least the range of 1 ng/m^3 to 50 ug/m^3.

The total sampling and analytical method was subjected to rigorous spike recovery tests under a variety of ambient conditions. The mean collection efficiency for Aroclor 1016/1242 was 101 ± 10 percent for sampling periods of 20 minutes to 12 hours and air volumes of 16 to 720 cubic meters. It is demonstrated that monochlorobiphenyl is the most difficult species to capture. A 2-hour sampling duration is the maximum that may be employed to quantitatively capture monochlorobiphenyl.

Dichlorobiphenyl and more highly substituted species may be quantitatively captured using up to 6-hour sampling periods. Data is presented to show that the analysis of the final one-third section of the polyurethane foam collection medium is a direct and reliable method of estimating system collection efficiency under specified system operating conditions.

Field tests of the method were conducted under a variety of ambient conditions including both low and high PCB levels. Typical ambient airborne PCB data is presented and discussed. In most locations the PCB that is collected does not closely resemble a single or a simple mixture of Aroclor; hence, perchlorination is required for quantitation. In locations near known or suspected sources of PCB, where high ambient levels are detected, Aroclor patterns are generally discernable and pattern matching techniques of quantitation may be employed.

The proposed method is recommended for the analysis of ambient airborne PCB. Both laboratory and field tests have demonstrated that the analyst may apply this method with a reasonably high degree of confidence in the resulting data. The accumulation of additional ambient data and additional experience in practical application will provide for a continuing evaluation of the method under an ever expanding range of conditions.

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APPENDIX A

METHOD FOR POLYCHLORINATED BIPHENYL (PCB) IN AIR

METHOD FOR
POLYCHLORINATED BIPHENYL (PCB) IN AIR

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OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

and

OFFICE OF TOXIC SUBSTANCES
ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Contract 68-01-2978
October, 1977

The mention of trade names of commercial products and suppliers in this procedure is for purposes of illustration only, and does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

METHOD FOR POLYCHLORINATED BIPHENYL (PCB) IN AIR

1.0 Principle of the Method

Airborne polychlorinated biphenyl (PCB) is collected on porous polyurethane foam by use of a modified high-volume (hi-vol) air sampling device.(1) The PCB is extracted from the polyurethane with an organic solvent. Chlorinated pesticides and other interferences are removed by column chromatography prior to gas chromatographic (GC) analysis using an electron capture (EC) detector. When a typical PCB pattern is not recognizable, analysis is performed by perchlorination of all PCB to decachlorobiphenyl (DCB) and subsequent quantitation as DCB. When biphenyl is present, or to demonstrate the absence of biphenyl, GC/FID (flame ionization detector) analysis is required to correct the analytical results for this non-chlorinated species. Figure 1 summarizes the steps this method entails.

2.0 Range of the Method

A detection limit of 1 ng/m^3 of PCB reported as DCB is achievable using a four-hour sampling period. The upper limit of the method is in excess of 50 ug/m^3 for short sampling periods (e.g., 20 minutes).

3.0 Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interference under the conditions of this analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems is required.

3.2 Toxaphene, phthalate esters, DDE, and polychlorinated naphthalenes can cause interferences with the determination of PCB if they are present.

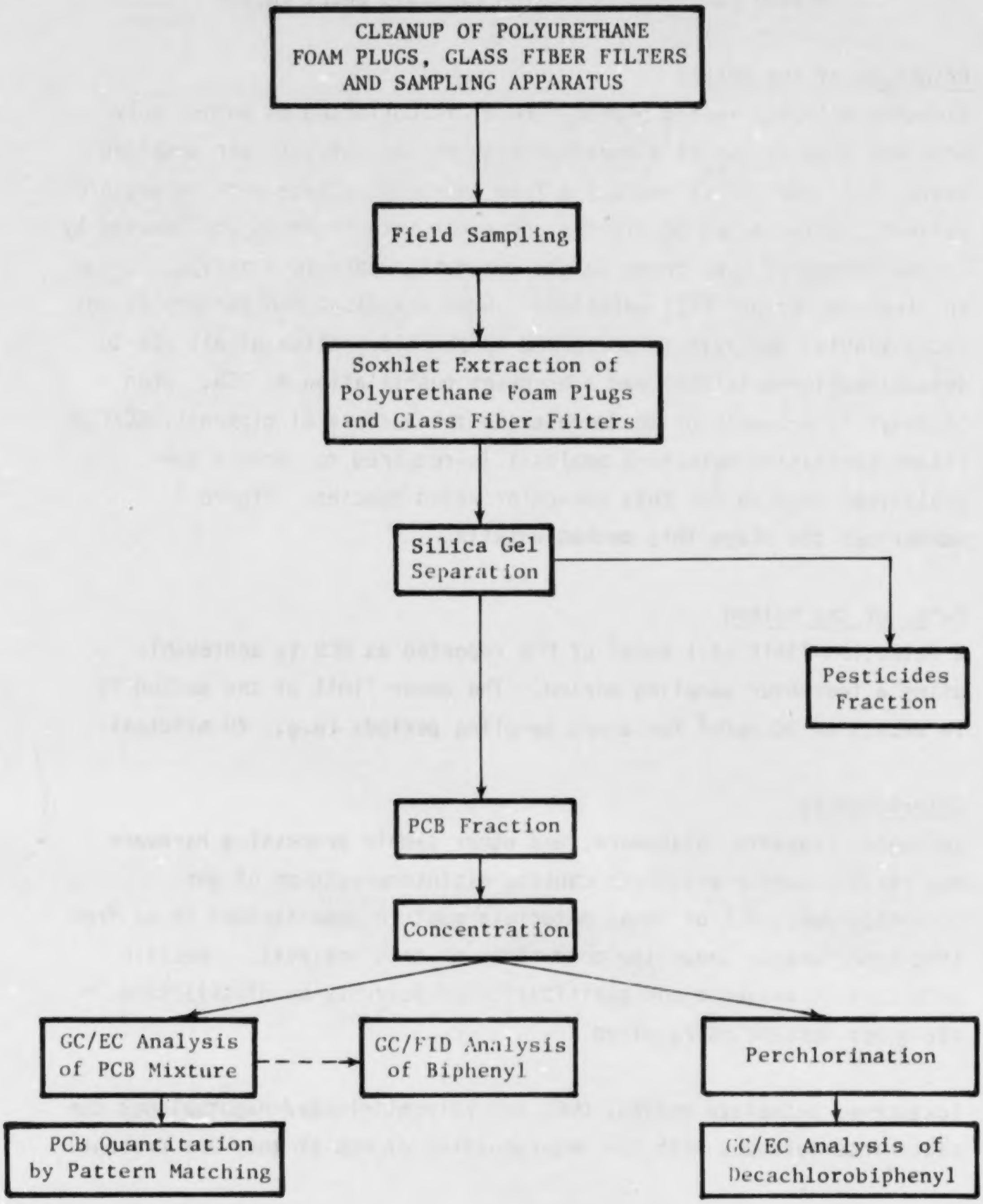
CLEANUP OF POLYURETHANE FOAM PLUGS, GLASS FIBER FILTERS AND SAMPLING APPARATUS
Field Sampling
Soxhlet Extraction of Polyurethane Foam Plugs and Glass Fiber Filters
Silica Gel Separation
Pesticides Fraction
PCB Fraction
Concentration
GC/EC Analysis of PCB Mixture
GC/FID Analysis of Biphenyl
Perchlorination
PCB Quantitation by Pattern Matching
GC/EC Analysis of Decachlorobiphenyl

Figure 1. Analytical Scheme for PCB in Ambient Air

4.0 Precision and Accuracy

4.1 Analytical. A test of the perchlorination methodology using both Aroclor 1016[a] and a PCB mixture containing monochlorobiphenyl, dichlorobiphenyl, and trichlorobiphenyl was conducted over the range of 0.103 ug/ml to 10.0 ug/ml. Eighteen analyses were performed. The mean percent conversion of PCB to DCB was 100 ± 4 percent over this range. A ruggedness test(2) of the perchlorination method indicated interlaboratory results obtained by competent trace analytical chemists should be readily comparable using this method.

4.2 Sampling. The recovery during tests of the method using Aroclor 1016 and Aroclor 1242 spiked onto the glass fiber filter that preceeds the polyurethane foam (PUF) collection media in the sampling device (see Figure 2), averaged 101 ± 12 percent over the range of 1.25 ug to 112 ug employing sampling periods between 20 minutes and 12 hours. Three PUF plugs were used at an average air flow rate of 0.8 m^3/min.

5.0 Apparatus, Materials, Instrumentation, and Reagents

5.1 Sampling Apparatus and Materials.

5.1.1 Modified hi-vol air sampler described in Section 6.3 (Figures 2 and 3)[b].

5.1.2 Variable voltage controller to adjust flow rate of hi-vol sampler.

5.1.3 Rotometer for measuring hi-vol flow rate[c].

---

a. Aroclor 1016® is a commercial product containing dichlorobiphenyls trichlorobiphenyls, and tetrachlorobiphenyls.

b. Basic unit may be obtained from General Metals Works, Cleves, OH. This unit is recommended for total suspended particulate sampling (Code of Federal Regulations, Title 40, Part 50, pp. 12-16, July 1, 1975).

c. May be obtained from: Dwyer Instruments, Inc., P.O. Box 618,
Marietta, GA 30061

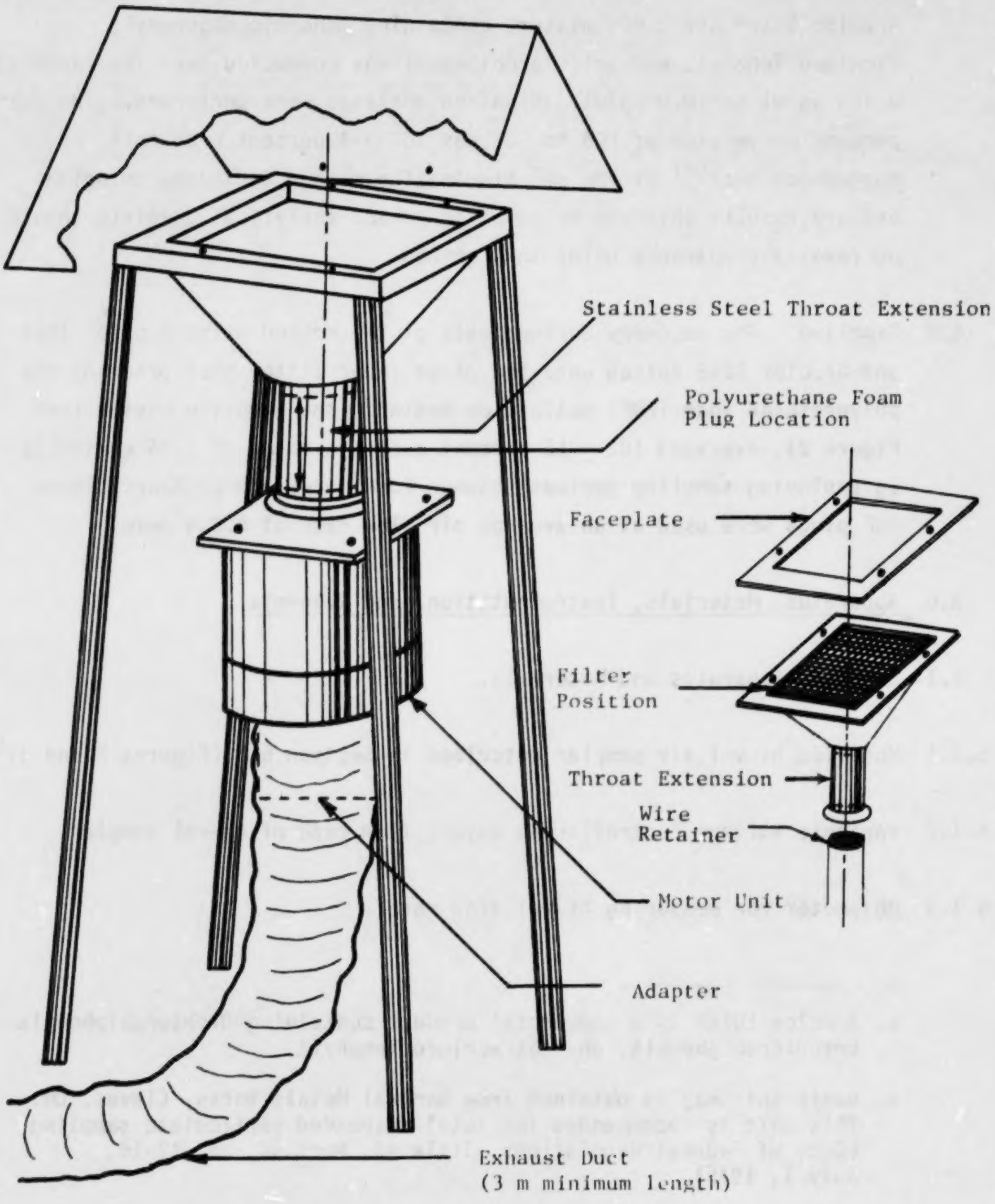
Stainless Steel Throat Extension
Polyurethane Foam Plug Location
Faceplate
Filter Position
Throat Extension
Wire Retainer
Motor Unit
Adapter
Exhaust Duct (3 m minimum length)

Figure 2. Assembled sampler and shelter with exploded view of the filter holder.

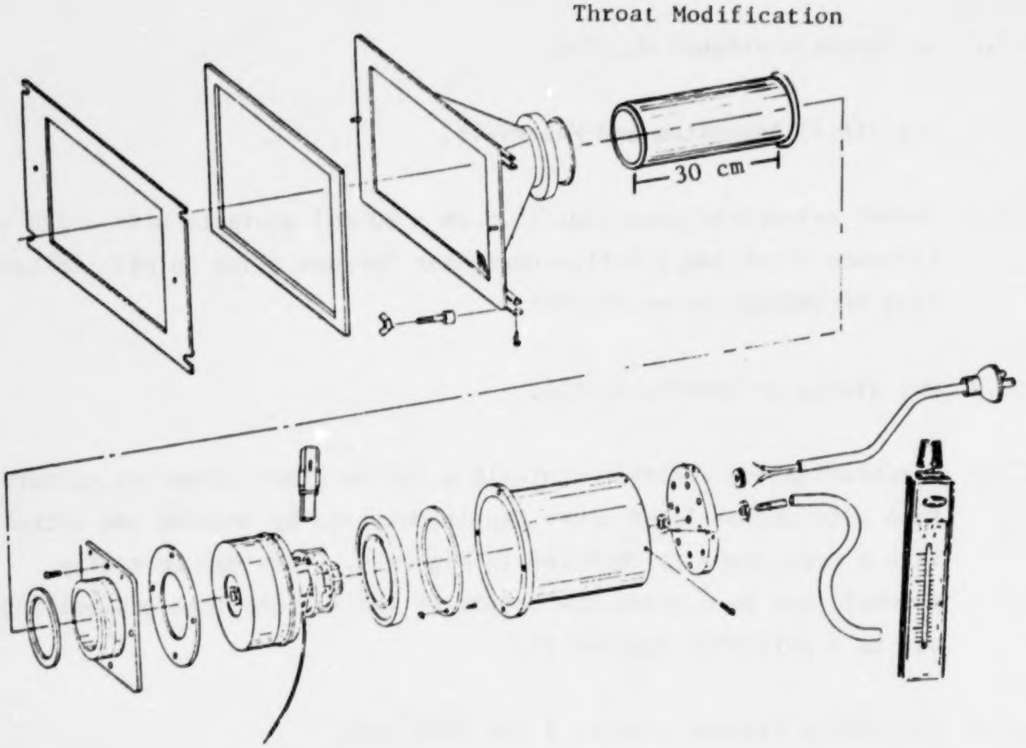
Throat Modification
30 cm

Figure 3. Exploded view of hi-vol sampling apparatus designed for use with a rotometer showing modified throat to accomodate polyurethane foam plugs.

5.1.4 Glass fiber filters (Gelman Type A, 25 cm x 20 cm).

5.1.5 Polyurethane foam. Three inch thick sheet. Density of 0.025 g/cc[d].

5.1.6 Glass jars (e.g., one pint fruit jars) suitable for storage and transport of the polyurethane foam plugs.

5.1.7 Collapsible exhaust ducting.

5.2 Analytical Apparatus and Materials.

5.2.1 Soxlet extraction apparatus (5.5 cm x 20 cm) equipped with a 300 ml florence flask and a reflux condenser (ground glass joint)--Kontes[e] item #K-585000, or equivalent.

5.2.2 Hot plates or heating mantle.

5.2.3 Perchlorination reaction vial--16 x 100 mm glass screw top culture tube with teflon-lined screw cap is modified by drawing the bottom into a cone shape as depicted in Figure 4. This may be easily accomplished by heating the bottom of the culture tube and pulling it out to a uniformly tapered tip.

5.2.4 Disposable Pasteur pipets--5 3/4 inch long.

5.2.5 Glass boiling beads--2 mm diameter.

5.2.6 Aluminum block tube heater--capable of maintaining a temperature of 160 ± 3°C. Suitable to receive reaction vials (Section 5.2.3).

---

[d] May be obtained from: Flexible Foam Products, Grand Sheet Metal Products Co., 1101 W. Wisdom St., Chattanooga, TN 37406, Product # 1636

[e] Kontes Glass Co.
Vinland, NJ

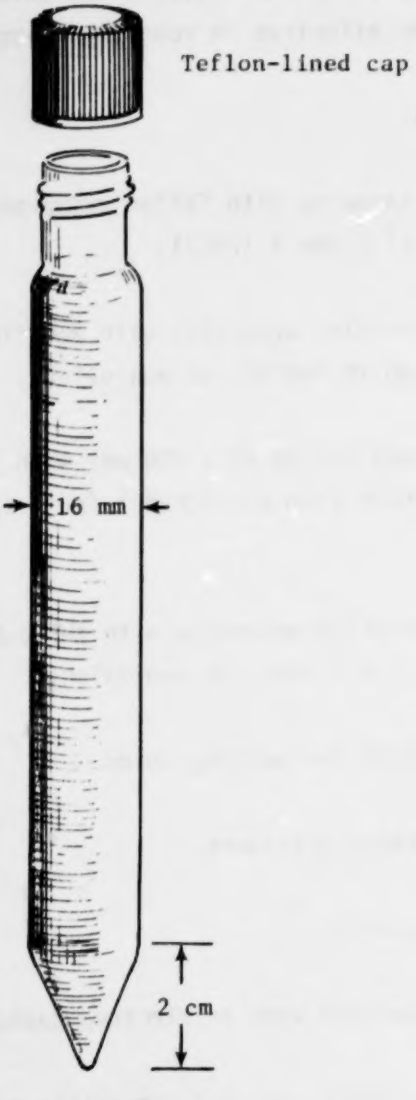
Teflon-lined cap
16 mm
2 cm

Figure 4. Perchlorination reaction vial.

5.2.7 Gas flow meter--range of 50-500 ml/min.

5.2.8 N_2 organic removal filter--organic contamination of compressed N_2 has been shown to be a problem. A filter constructed as shown in Figure 5 has been found to be effective in removing these organic contaminants.

5.2.9 Syringe--1 to 10 ul.

5.2.10 Hypo-vials®--10 ml capacity with Teflon crimp-on septa. May be obtained from Pierce[f] (item # 12903).

5.2.11 Kuderna-Danish evaporating apparatus with modified micro-Snyder condenser-Kontes item #K-569250, or equivalent.

5.2.12 Chromatographic column (13 mm OD x 250 mm) with 200 ml reservoir and teflon stopcock (Kontes item # K-420280) for preparation of silica gel column (10.21).

5.2.13 Kuderna-Danish evaporating apparatus with three-ball macro-Snyder column--Kontes item # K-570000, or equivalent.

5.2.14 Hengar® granules, micro for boiling chips.

5.2.15 Miscellaneous laboratory glassware.

5.3 Analytical Instrumentation.

5.3.1 Gas chromatograph equipped with an electron capture detector.

5.3.2 Potentiometric strip chart recorder compatible with the gas chromatographic detector system.

---

[f] Pierce
Box 117
Rockford, IL 61105

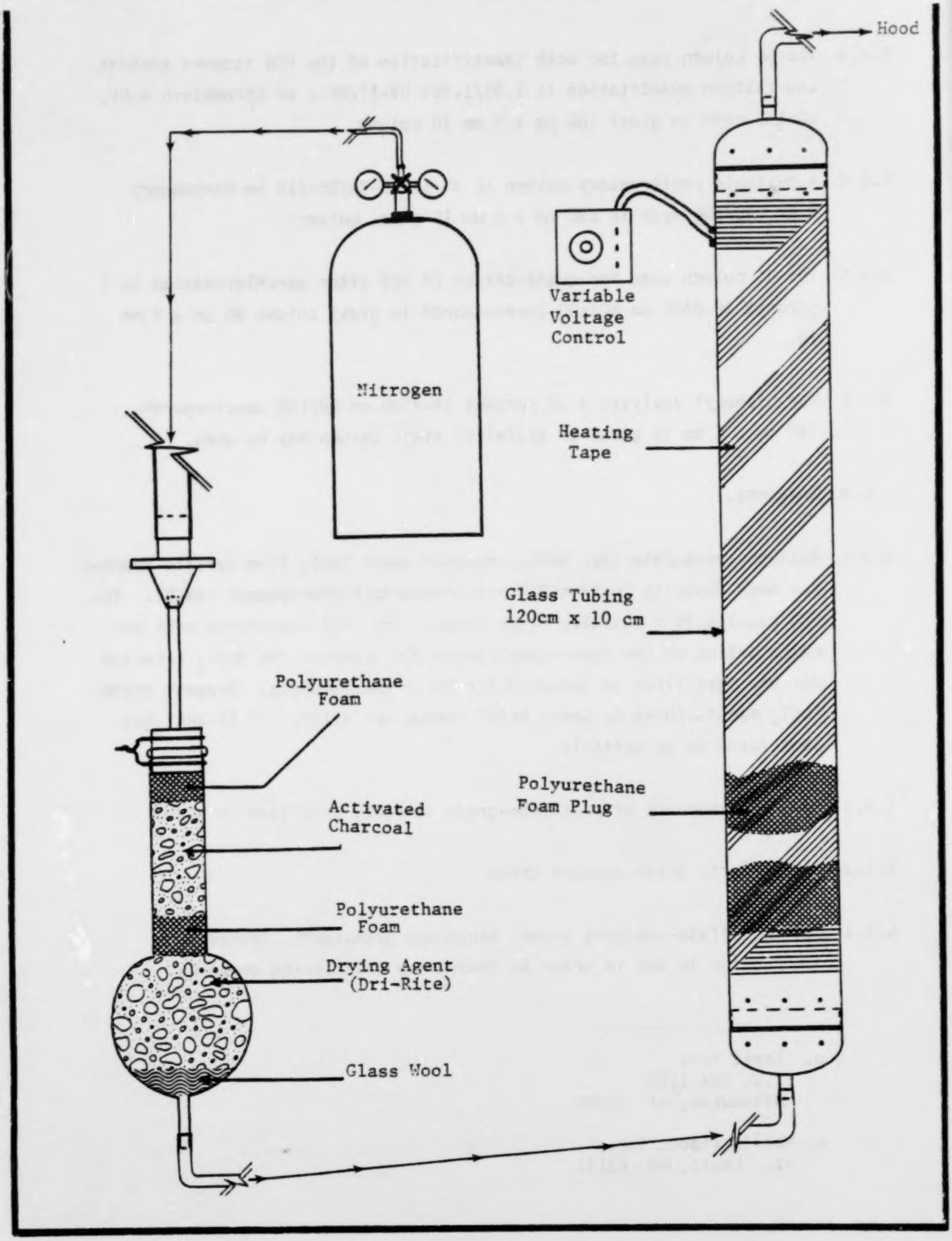
Hood
Variable Voltage Control
Nitrogen
Heating Tape
Glass Tubing 120cm x 10 cm
Polyurethane Foam
Activated Charcoal
Polyurethane Foam Plug
Polyurethane Foam
Drying Agent (Dri-Rite)
Glass Wool

Figure 5. Apparatus for drying polyurethane foam plugs.

5.3.3 The GC column used for both identification of the PCB isomers present and pattern quantitation is 1.5%/1.95% OV-17/QF-1 on Chromosorb W-HP, 80/100 mesh in glass 180 cm x 2 mm ID column.

5.3.4 A suitable confirmatory column is 4%/6% SE-30/OV-210 on Chromosorb W-HP, 80/100 mesh in 180 cm x 2 mm ID glass column.

5.3.5 The GC column used for quantitation of DCB after perchlorination is 3 percent SP-2401 on 80/100 Supelcoport® in glass column 90 cm x 2 mm ID.

5.3.6 For biphenyl analysis a 10 percent SP-2100 on 80/100 Supelcoport®, 180 cm x 2 mm ID glass or stainless steel column may be used.

5.4 Reagents.

5.4.1 Antimony pentachloride, $SbCl_5$--reagent grade $SbCl_5$ from certain sources has been found to contain DCB and bromonanochlorobiphenyl (BNCB). The DCB results in a positive blank value. The BNCB interferes with perchlorination of the lower-substituted PCB isomers. The $SbCl_5$ selected for use must first be analyzed for these contaminants. Reagent grade $SbCl_5$ manufactured by Cerac Pure[g] (stock no. A1147, lot 15-26A) has been found to be suitable.

5.4.2 Hexane--nanograde or pesticide-grade solvent, distilled in glass.

5.4.3 Hydrochloric acid--reagent grade.

5.4.4 Sodium sulfate--reagent grade, anhydrous granular[h]. Heated to 300°C prior to use in order to remove any interfering organics.

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[g] Cerac Pure
P.O. Box 1128
Milwaukee, WI 53201

[h] Mallinckrodt, Inc.
St. Louis, MO 63147

5.4.5 Compressed nitrogen--water pumped and pre-purified to 99.99% pure.

5.4.6 Decachlorobiphenyl (DCB)--pure DCB isomer for quantitation purposes may be obtained from Analabs, Inc.[i] (Stock #RCS-051) or from RFR Corp.[j] (Stock #RCP-28).

5.4.7 Chromatographic grade silicic acid (100 mesh)--Woelm[k] silica gel activity grade I.

5.4.8 Aroclor standards and biphenyl--may be obtained from Analabs, Inc. or from EPA Pesticide Repository (MD-69), Research Triangle Park, North Carolina 27711.

6.0 Preparation of Materials and Equipment

6.1 Polyurethane foam absorbent media.

6.1.1 Circular plugs of diameter 8.9 cm are cut from 7.6 cm thick sheet polyurethane foam. These plugs will fit snuggly into the throat of the modified hi-vol sampler (Figure 2). A cutting device as depicted in Figure 6 has been found suitable for cutting highly uniform polyurethane foam plugs from the stock material. This device was manufactured by removing the internals and bottom of an automobile oil filter of the correct dimensions and buffing a cutting edge. A bolt is attached as shown in Figure 6 to allow attachment to a drill chuck. Using a reasonably slow drill speed, this device is used to cut through the sheet polyurethane foam. Lubricate the cutting edge constantly during cutting with a fine stream of water.

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[i] Analabs, Inc.
80 Republic Drive
New Haven, CT 06473

[j] RFR Corporation
1 Main Street
Hope, RI 02831

[k] May be obtained from: ICN Pharmaceuticals, Inc.
Life Science Group
26201 Miles Road
Cleveland, OH 44128

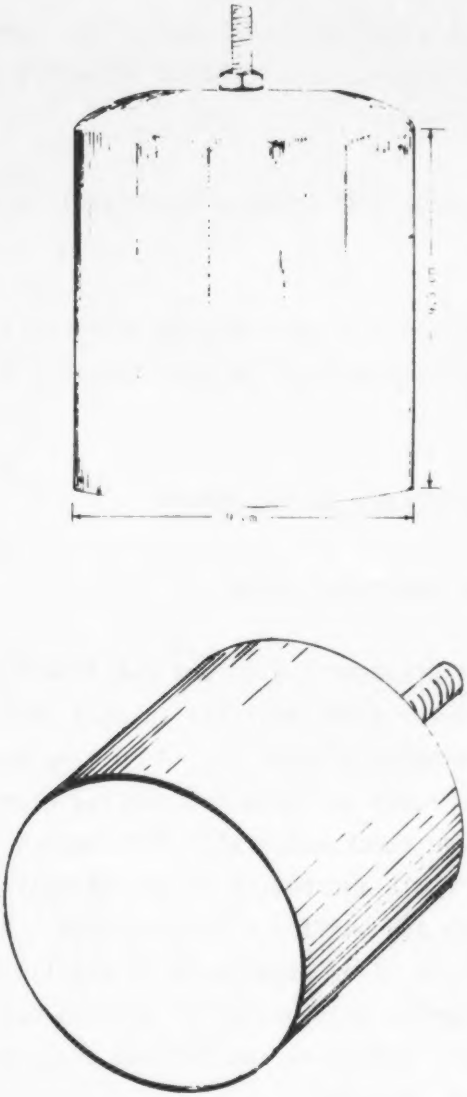

Figure 6. Polyurethane Foam Cutting Device

6.1.2 To remove contaminating organics, extract each polyurethane foam plug for twelve hours with hexane in a soxhlet extraction apparatus (Section 5.2.1).

6.1.3 Dry the extracted polyurethane foam plugs with organic-free N_2. A glass cylinder (10 cm diameter) wrapped with heating tape and fitted with a N_2 inlet and exhaust as depicted in Figure 5 has worked well for the drying of many plugs at one time.

6.1.4 Avoid exposure of cleaned foam plug to laboratory atmosphere to prevent contamination with PCB.

6.1.5 Store each polyurethane foam plug in a wide-mouth, solvent-rinsed glass container with pre-cleaned aluminum foil between jar and cap. The aluminum foil is heated to 200°C for at least one hour before use to remove organics.

6.2 Glass Fiber Filters.

6.2.1 Gelman Type A (20 cm x 25 cm) glass fiber filters are heated to 200°C for several hours to remove contaminating organics. They are then wrapped in pre-heated aluminum foil until use. After use they are returned to the aluminum foil wrappers for transport to the laboratory.

6.3 Hi-vol Sampling Device.

6.3.1 Standard hi-vol air samplers are modified by the addition of a 30 cm stainless steel extension to the throat section of the assembly as shown in Figures 2 and 4. Air flow rate of this device can be varied from approximately 0.5 m^3/min to 1.5 m^3/min by use of a potentiometric speed controller.

6.3.2 A wire or screen retainer as shown in Figure 2, is placed between the polyurethane foam plugs in the throat of the apparatus and the motor unit to prevent movement of the plugs during sampling.

6.3.3 To avoid the possibility of contamination of interfering organic substances, the neoprene seal around the perimeter of the filter faceplate is removed. A seal is maintained by wrapping the faceplate with Parafilm®.

6.3.4 An exhaust duct 5 meters or more in length, of collapsible ducting material is placed on the hi-vol exhaust and is positioned downwind during sampling to avoid recirculation of air through the sampler.

7.0 Sample Collection

7.1 A 20 cm x 25 cm glass fiber filter (Gelman Type A) is mounted in the high-volume sampling apparatus.

7.2 Three foam plugs (Section 6.1.1) are inserted into the 8.2 cm diameter throat of the high-volume sampling apparatus, taking care to avoid empty spaces between the plugs and cylinder wall.

7.3 The hi-vol air flow rate is adjusted to 0.8 ± 0.2 m^3/min using the rotometer (see Figure 3). Flow is measured at the beginning and end of each sampling period and the volume of air sampled is calculated as follows:

$$V = \frac{Q_i + Q_f}{2} \times t$$

where, V = air volume sampled (uncorrected), m^3
Q_i = initial air flow rate, m^3/min.
Q_f = final air flow rate, m^3/min.
t = sampling time, min.

Rotometer calibration procedures are described in (3).

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7.4 A sampling period is selected which is commensurate with the expected airborne PCB level. Under normal circumstances, a two-hour period is appropriate for airborne levels of 2 ng/m^3 or greater. If levels are expected to be lower (i.e., less than 2 ng/m^3), a six-hour sampling period is recommended. If the sampling period is too long for higher airborne levels, PCB may pass through the collection media with consequently lower collection efficiency. If the sampling period is not long enough for the ambient levels present, detectable quantities may not be collected. Tests have demonstrated that all PCBs, including monochlorobiphenyl, are effectively retained over a two-hour sampling period and that dichlorobiphenyl is effectively retained over a six-hour sampling period. Aroclor 1242 is retained in excess of 12 hours at normal sampling rates.

7.5 The sampling apparatus is rinsed between sample runs with hexane to remove any PCB contamination.

8.0 Sample Extract Preparation

8.1 After sampling is completed, the filters are removed, and refluxed for three hours with 300 ml hexane in a soxhlet extractor. The first and second polyurethane foam plugs, as located in the sampler with respect to air flow, are extracted for three hours (18 cycles) in a soxhlet extractor (Section 5.2.1) with 200 ml hexane. The extracts are combined and concentrated to 5 ml in a Kuderna-Danish apparatus (Section 5.2.13).

8.2 Chromatographic Separation of Chlorinated Pesticides.

8.2.1 A silica gel column is prepared by wet packing in hexane about 3 g of the dry activated absorbent previously cleaned in benzene and dried to 200°C for four hours. Draw off excess hexane used to make this slurry and wash the column with 50 ml of hexane. A 250 mm x 13 mm column is used (Section 5.2.12).

8.2.2 Place 2 g of anhydrous Na_2SO_4 on top of the cilica gel column to remove any water from the sample extract.

8.2.3 The hexane extract of 5 ml is quantitatively transferred to the column, rinsing the Kuderna-Danish receiver three times with a small amount of hexane.

8.2.4 Allow the sample to drain through the column until the liquid level is about 0.5 cm above the top of the Na_2SO_4.

8.2.5 Elute the PCB fraction with 50 ml of hexane, collecting all hexane in a clean, graduated Kuderna-Danish receiver (Section 5.2.13). Most chlorinated hydrocarbon pesticides (except DDE) are retained on the column and may be eluted with benzene if analysis is desired.

8.3 The eluate is concentrated to 5 ml in the Kuderna-Danish apparatus (Section 5.2.13). A modified micro-Snyder column is then attached to the receiver (Section 5.2.11) and the solution is evaporated to less than 1.0 ml using the graduations on the evaporator receiver. Care must be taken not to evaporate to dryness or the more volatile PCB species will be lost.

8.4 Bring the volume up to the 1.0 ml graduation mark on the Kuderna-Danish evaporator receiver with fresh hexane. The extract is now ready for either GC/EC analysis and quantitation by Aroclor pattern matching or derivitization to DCB followed by GC/EC quantitation.

8.5 If the sample is to be stored at this point, the extract should be quantitatively transferred to a Hypo-vial without a significant evaporative loss of solvent. Close the Hypo-vial with teflon septum and aluminum cap (Section 5.2.10).

9.0 Analysis and Quantitation of PCB

Two techniques are available for the quantitation of PCB; the Aroclor pattern matching technique and perchlorination. The analyst must decide which of these techniques to use based on the appearance of the chromatograms. Airborne PCB may or may not exhibit a GC elution pattern that matches an Aroclor elution pattern. Given a source of Aroclor, the relative volatilities of the various species will vary widely resulting, generally, in a bias of the GC pattern toward the more volatile species as compared to an Aroclor standard prepared in solvent.(4) This will be particularly true of ambient airborne samples taken at a considerable distance from the source or sources, since differential rates of transport among the various species can exert a significant effect. Most ambient air samples exhibit a large amount of apparent PCB which is early eluting. It is extremely difficult to match these early eluting peaks to a standard Aroclor elution pattern. These early eluting peaks may represent a highly significant amount of PCB. Hence, it is recommended in most cases that the perchlorination method be used for PCB quantitation and confirmation. If it is of interest to know the PCB species present, the sample should be analyzed by comparison with Aroclor or specific isomer PCB standards before perchlorination. Biphenyl, if present, may be analyzed by GC/FID. In those cases where the chromatogram closely matches an Aroclor pattern, the pattern matching technique is recommended. Experience has shown this is a suitable method for the higher ambient airborne levels observed near known sources of PCB.

10.0 Identification and Quantitation of PCB Mixture by Pattern Matching

10.1 Analyze the hexane extract on a 1.5/1.95% OV-17/QF-1 column. The following conditions have been found to be suitable:

Glass column, 180 cm length, 3 mm ID
1.5%/1.95% OV-17/QF-1 liquid phase
Chrom W-HP, 80/100 mesh support
N_2, 35 psig inlet pressure
Detector temperature--220°C
Column temperature--200°C
Injector temperature--245°C
Detector--electron capture

10.2 The analyst may qualitatively assess the species distribution of the PCB present by comparison of the GC elution pattern with that of an Aroclor or a series of various Aroclor standards, or, if desired, with individual PCB species.

10.3 Once the elution pattern is subjectively matched to a standard Aroclor pattern, quantitation is conducted by integration of peak areas or comparison of peak height. The methodology for quantitation by pattern matching is described by Chan and Sampson (5) and by the U.S. Environmental Protection Agency (6)(7). Care must be taken to insure that the sample chromatogram and the standard chromatogram are close to the same concentration (i.e., they may differ by no more than a factor of 2). This is necessary to assure the EC detector is operating in a linear range.

10.4 For purposes of confirmation of the PCB present, an SE-30/OV-210 column may be used with the following operating conditions:

Glass column 180 cm length, 2 mm ID
4%/6% SE-30/OV-210 liquid phase
Chromosorb W-(HP), 80/100 mesh support
N_2, 38 psig inlet pressure
Detector temperature--225°C
Column temperature--200°C
Injector temperature--240°C
Detector--electron capture

11.0 Method for Quantitation of PCB by Perchlorination

11.1 Principal. Perchlorination of a PCB mixture using antimony pentachloride ($SbCl_5$) as the active reagent results in conversion of all PCB present to DCB which is a single isomeric, fully-substituted species.(8) This species has a high electron capture (EC) detector response. It can also be more readily separated from other compounds by GC techniques than can the complex PCB mixture. Quantitation can be accomplished by measurement of a single peak.

11.2 Sample Preparation. The sample extract (1.0 ml) prepared in the method described above is quantitatively transferred to a Kuderna-Danish apparatus with micro-Snyder column (Section 5.2.13).

11.3 Removal of Solvent. The extracted PCB must be quantitatively exchanged from the hexane solvent to chloroform. All residual hexane must be removed from the extract prior to perchlorination. Even small amounts of residual hexane will result in the formation of a black solid residue upon the addition of $SbCl_5$. This severely reduces PCB recovery. The hexane is removed by azeotrophic evaporation from the hexane/chloroform mixture.

11.3.1 Add 3 ml of nanograde chloroform to the Kuderna-Danish receiver containing the sample extract in hexane and concentrate, using a micro-Synder column, by slow boiling in a tube heater or water bath to about 0.2 ml. Do not allow to evaporate to dryness.

11.3.2 Repeat step 11.3.1 three additional times in order to remove all residual hexane. Rinse the micro-Snyder apparatus with a minimum amount of chloroform. Final volume should be approximately 1.0 ml.

11.3.3 Quantitatively transfer to a reaction vial (Section 5.2.3) using three chloroform rinses (Total rinse volume about 2 ml).

11.3.4 Add two micro-Hengar boiling chips and immerse reaction vial upright in a 70°C water bath to a depth of 6 ± 2 cm.

11.3.5 Increase water bath temperature slowly until the solvent begins to boil. Boiling temperature should be 72-76°C.

11.3.6 Concentrate slowly to a volume of approximately 0.1 ml. Under no circumstances should the water bath temperature be permitted to exceed 76°C or the solvent will be evaporated to dryness. If either of these happen, PCB will be lost by volatilization and consequent recoveries will be low. The final volume (0.1 ml) may be determined with sufficient accuracy by comparison of solvent level with another reaction vial containing 0.1 ml of chloroform.

11.3.7 When a volume of 0.1 ml is achieved, cap the reaction vial immediately and allow to cool.

11.4 Sample Perchlorination.

11.4.1 To the concentrated sample extract in the reaction vial add 0.2 ml of $SbCl_5$ (Section 5.4.1) and immediately re-seal the vial tightly with the Teflon-lined screw cap.

11.4.2 Place the reaction vial into a preheated (160 ± 3°C) aluminum block heater for a period of 15 hours.

11.4.3 After the reaction period, remove the reaction vial from the aluminum block heater and allow to cool to room temperature. Then cool to 0°C in an ice water bath.

11.4.4 Cautiously vent pressure from the vial in a fume hood, directing away from the analyst. Add 1 ml of 6 N HCl to the cool reaction vial, replace the cap tightly and shake for 30 seconds. The HCl stops the perchlorination reaction. CAUTION: IF THE REACTION VIAL IS NOT COOL, THE ADDITION OF HCl MAY CAUSE DANGEROUS SPLATTERING OF THE REAGENTS FROM THE CONTAINER.

11.4.5 Add 1 ml hexane, shake vigorously for 30 seconds and carefully draw off the hexane layer with a disposable pipet.

11.4.6 Place this hexane extract on the top of a 6 mm x 12 cm disposable pipet packed with 2 g of anhydrous Na_2SO_4. This column is prewashed with hexane.

11.4.7 Repeat steps 11.4.5 and 11.4.6 five times to assure complete extraction of all DCB from the reaction vial.

11.4.8 Pass two 1 ml portions of fresh hexane through the Na_2SO_4 column and collect all fractions in a 10 ml graduated Kuderna-Danish receiving vial (Section 5.2.11).

11.4.9 Connect a modified micro-Snyder column to the Kuderna-Danish apparatus (Section 5.2.11), add one Hengar boiling chip, and evaporate in a water bath (70°C) to less than 0.5 ml. Care must be taken to avoid bumping and loss of sample.

11.4.10 Cool the apparatus to room temperature and remove the micro-Snyder column. Rinse the micro-Snyder column with sufficient fresh hexane to bring the volume up to 1.0 ml as indicated on the graduated Kuderna-Danish receiving vial. Remove the micro-Snyder column and mix by gentle swirling.

11.4.11 Transfer the extract immediately (before significant solvent evaporation) to a properly-labeled Hypo-vial.

11.4.12 Close the Hypo-vial with a Teflon septum and aluminum cap (Section 5.2.10). All PCB present in the sample has been converted to DCB in 1.0 ml hexane. The sample is now ready for GC analysis.

11.5 Analysis

11.5.1 Analyze the DCB present in the perchlorinated extract by GC/EC. The following column conditions have been found to be suitable:

Glass column: length 6 ft., ID 1/8"
1.5% OV-17/1.95% QF-1 liquid phase
Chromosorb W-HP, 80/100 mesh support
N_2, 35 psig inlet, approximately 40 ml/min

Column temperature--220°C
Injection port temperature--240°C
Detector Temperature--200°C

Under these conditions, DCB will elute in approximately 20 minutes. Figure 6 is a typical chromatogram.

11.5.2 A procedural blank value must be determined with which to correct low level analytical results. Select two PUF plugs and a glass fiber filter that have been cleaned-up and handled in the same manner as the materials used for air sampling. Extract these PUF plugs and filter in the same manner as described above for the samples. Perchlorinate the extracts in the same manner as an air sample. The resulting blank concentration, if significant, must then be used in the calculation of airborne PCB concentration. It has been found that the lowest procedural blank value achievable is approximately 50 ng of DCB after perchlorination. This amount is readily detectable. The minimum detectable airborne concentration should, therefore, be considered to be in the range of 100 ng as DCB.

11.5.3 Quantitate as DCB by comparison of the peak area with that of a known concentration of pure DCB (Section 5.4.6) taking into consideration all concentration factors. Care must be taken to assure the sample concentration and the standard concentration are near the same value so the EC detector is operating in the linear range. Peak areas of the standard and the sample should not differ by more than a factor of two.

$$\text{ng DCB/m}^3 = \frac{\frac{A - B}{S} \times C}{V}$$

where A = area of the DCB peak of the sample
B = area of the DCB peak of the procedural blank (Section 11.5.2)
S = area of DCB standard peak
C = concentration of the DCB standard in ng
V = volume of air sampled in m^3.

11.5.4 To convert DCB values to approximate equivalent PCB values, Table 1 may be employed.

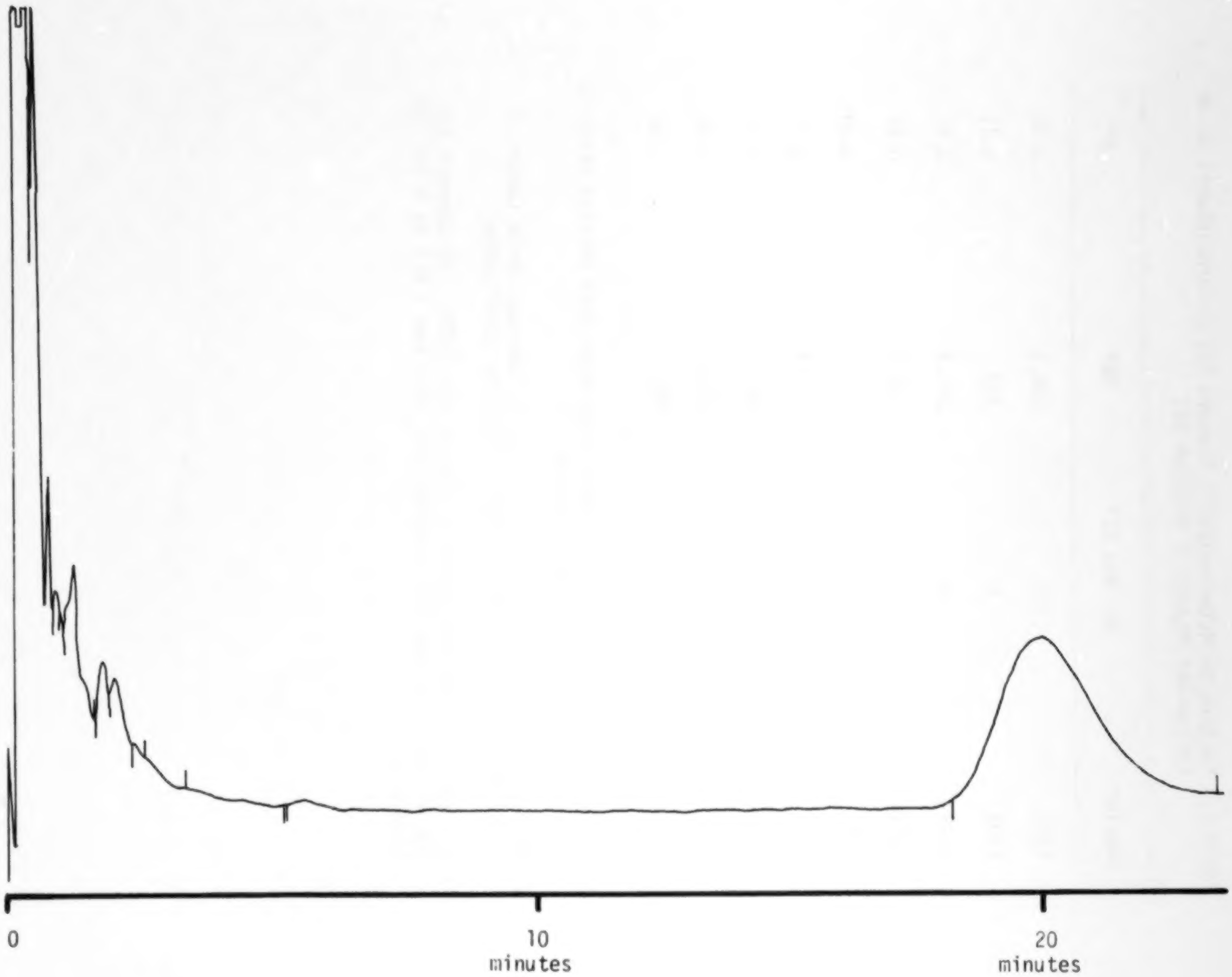

Figure 6. Typical Chromatogram Showing PCBs After Perchlorination [illegible]

Table 1. Factors to Mathematically Convert Decachlorobiphenyl to an Equivalent Amount of Aroclor (8)

Aroclor	Av. No. Cl*	MW†	X**
1221	1	188.5	0.38
1232	2	223	0.45
1242	3	257.5	0.52
1016	3	257.5	0.52
1248	4	292	0.59
1254	5	326.4	0.65
1260	6	361	0.72
1262	7	395.3	0.79
DCB	10	499	1.00

* Average whole mumber of chlorines calculated from percent chlorine substitution for a specific Aroclor

† Molecular weight of Aroclor based on the average whole number of chlorines calculated from percent chlorine substitution

** X = molecular wt Aroclor/molecular wt DCB (499). To convert ppm DCB to ppm of a specific Aroclor, multiply ppm x DCB by X for the Aroclor.

11.5.5 Confirmation may be accomplished by: a) gas chromatographic/mass spectroscopy if sufficient DCB is present, or b) analysis on an alternate GC column as suggested in Section 10.4.

12.0 Analysis of Biphenyl

12.1 Biphenyl is converted to DCB during the perchlorination step. If a significant amount of biphenyl is present in a sample, the analyst may want to correct the results for this. A separate GC analysis and quantitation using a flame ionization detector (GC/FID) is required.

12.2 Biphenyl may be analyzed on an SP-2100 column using the following operating conditions:

10% SP-2100 on 80/100 Supelcoport
180 cm x 2 mm ID stainless steel or glass column
Carrier gas: N_2 @ 27 ml/min
Detector: flame ionization, H_2 @ 22 psi
Temperature program: 134°C for 8 min. then increase to 150°C at 4°C/min. Elution temperature about 146°C. Elution time 10 min

12.3 If it is desired that the perchlorination result (total DCB) reflect only PCB in a sample that contains biphenyl as well as PCB, the analyst must correct the result as follows:

$$\text{Corrected ng DCB/m}^3 = \text{calculated ng DCB/m}^3 - \frac{Y}{0.307}(\text{ng BIPH/m}^3),$$

where Y is the conversion efficiency of biphenyl (BIPH) to DCB in the perchlorination procedure. Tests (N=10) have shown the value of Y is 0.443 ± 0.088 using the perchlorination technique described above.

13.0 Quality Control

13.1 The collection efficiency of the sampling system should be checked by independent extraction and analysis of the third PUF plug (the one farthest from the sampler intake). Comparison of the PCB collected on this plug to the total on the other two plugs provides an estimate of the collection efficiency of the sampling system if the sampling guidelines described in Section 7.4 are followed.

13.2 Approximately 10 percent of the sample extracts are analyzed in duplicate. Frequent material and reagent blank values are determined.

13.3 Extraction technique may be evaluated by spiking and recovery of PCB from the polyurethane foam.

13.4 The procedural blank value must be frequently determined (Section 11.5.2) and must be consistently low with respect to the PCB collected during sampling.

13.5 Standards are frequently injected as a check of the stability of the operating conditions, detector, and column.